VOL. LIII, NO. 2, FEBRUARY, 1958

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The Journal

of the

AMERICAN LEATHER CHEMISTS ASSOCIATION

Vol. LIII FEBRUARY 1958 No. 2

CONTENTS

A Case History of Statistical Quality Control in Chrome Tanning - *By* F. L. Collins and G. M. Oliensis 72

Tanning Studies with Dialdehyde Starch - - - - *By* E. M. Filachione, E. H. Harris, M. L. Fein, A. H. Korn, J. Naghski, and P. A. Wells 77

The Action of Acrylonitrile and Acrylamide upon Collagen - - - - *By* L. Seligsberger and H. Clayton 90

Studies of Leather Fungicides - - - - - - - - - - - - *By* S. Dahl and A. M. Kaplan 103

Life Lines - - - - - - - - - - - - 119

ALCA News - - - - - - - - - - - - 121

Abstracts - - - - - - - - - - - - 124

Book Review - - - - - - - - - - - - 130

SUBSCRIPTION - - MEMBERS $12.00 A YEAR - - NONMEMBERS $15.00

Published Monthly by

The American Leather Chemists Association

Entered as Second-Class Matter at the Post Office, Easton, Pa.
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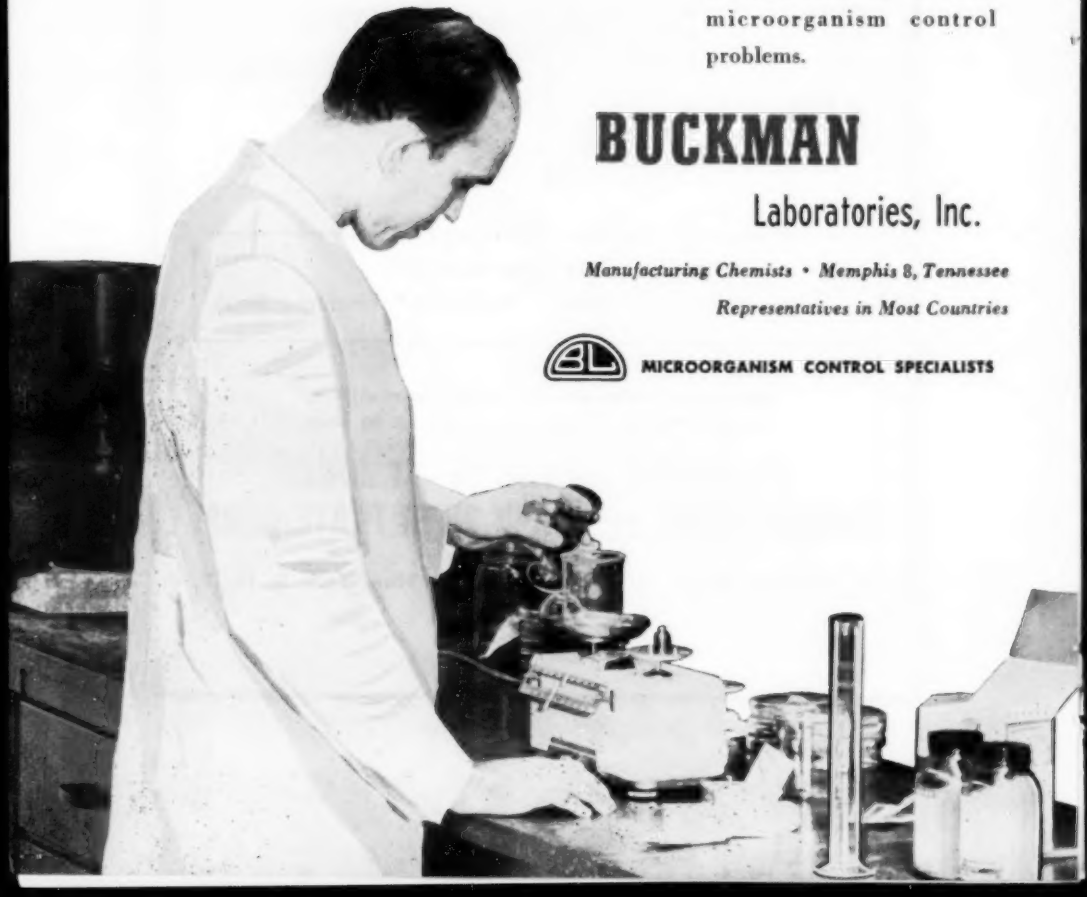

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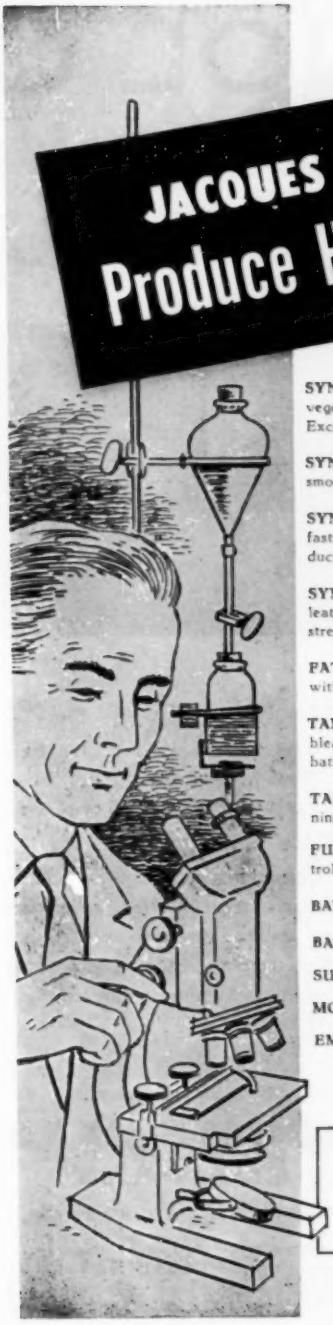

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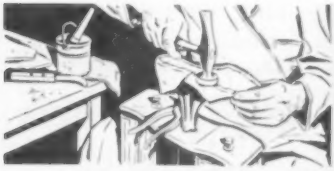

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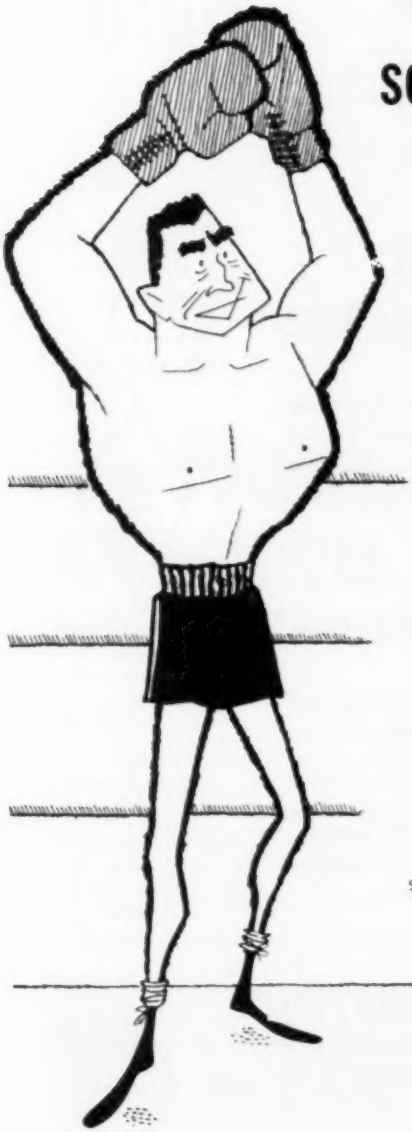

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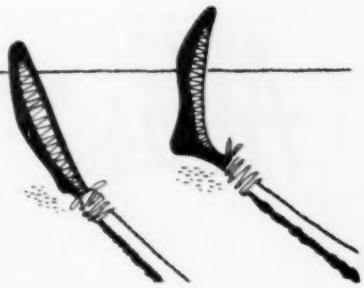

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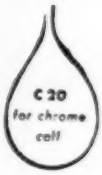

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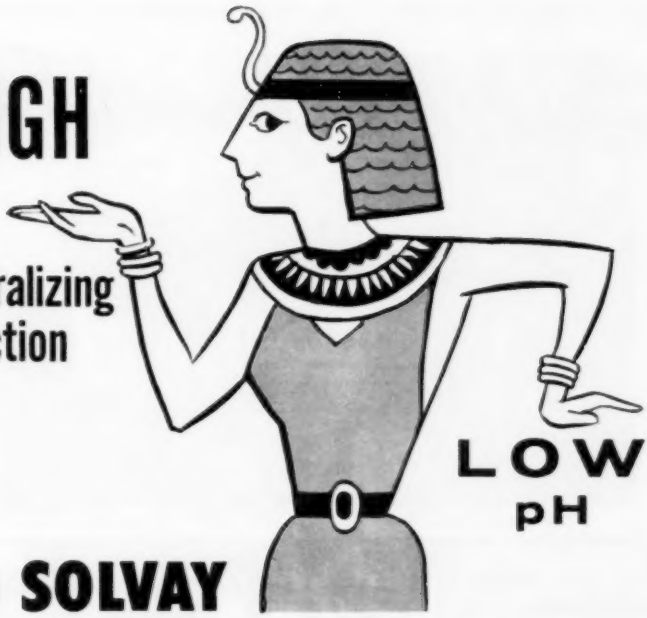

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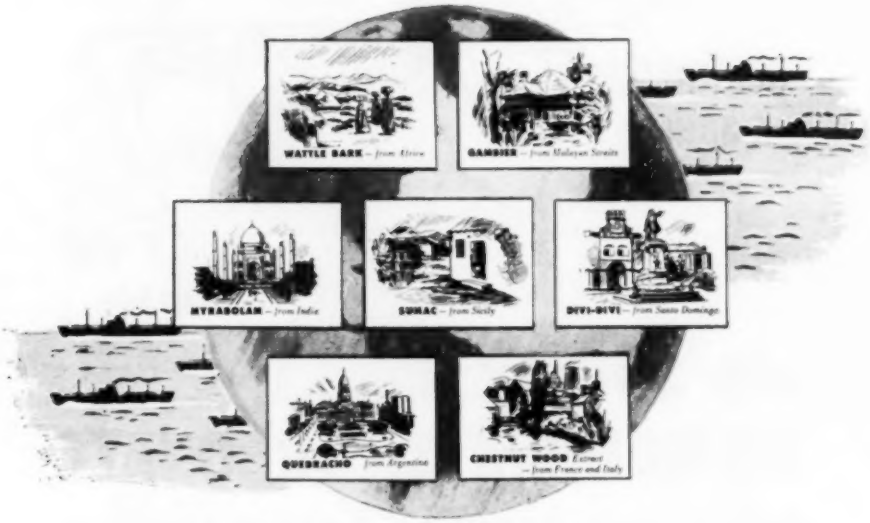
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General correspondence concerning the *Journal* should be mailed to the Managing Editor. Subscriptions—$12 per year for members; $15 for nonmembers.

A CASE HISTORY OF STATISTICAL QUALITY CONTROL IN CHROME TANNING*

F. L. Collins and G. M. Oliensis

International Shoe Company
St. Louis, Missouri

The use of shrinkage temperature as an index of chrome tanning is at least 50 years old. Statistical treatment of enumeration and measurement data is considerably older. Statistical Quality Control developed rapidly during and after World War II. Our introduction to this discipline, as applied to shrink temperature measurements, began in 1947. By 1948 a plant-wide procedure had been adopted.

Currently we have four chrome leather tanneries processing about 200,000 pounds of cattle hide daily. For control purposes some 200 shrink temperature measurements are made per day, i.e., about 1 hide in every 25 is tested. Using eight instruments, each capable of handling 6 specimens at a time, and a starting bath temperature of 185° F., about 8 man-hours per day are required for testing. The data are plotted on conventional control charts for the convenient information of supervisory personnel.

A decade of experience has convinced us that Statistical Quality Control of shrink temperature measurements makes a worth-while contribution to uniform quality. It has helped us in reducing both within-tannery and between-tannery variations. This paper summarizes some of our experiences.

We carefully sort in the hide house into 10 classifications in order to have lots containing hides of approximately the same area and thickness. We believe this helps to reduce variation within lots. The evidence indicates that there is some systematic difference between hide sorts. It is inconclusive at this time because the magnitude of the difference is relatively small.

We tan approximately 5,000 pounds of pickle stock in an 8-foot diameter drum. No difference has been found in the rate of tanning between speeds of 14 and 16 r.p.m., but a decided increase in rate occurs when going from 16 to 18 r.p.m. Our preferred leather is made by floating at 70° F., drumming 8 hours in 18-r.p.m. drums, and ending with a float temperature of 105° F.

Prior to 1948 our specification for chrome tanning called for "no shrinkage after one minute at 195° F." (The stock is later chrome retanned.) This "no-failure" type of test is of little value for control purposes since it will only detect an occasional, one-direction, gross error. A test of increased severity would be much better. Such a test would specify a certain time and

*Presented at the 5th Biennial Congress of the International Union of Leather Chemists' Societies, Rome, Italy, September 20, 1957.

temperature, say 10 minutes at the boil, after which some relatively large fraction, say 0.50, of all specimens tested will shrink, if the process is under control. This is an accredited Quality Control procedure capable of detecting a change of level in either direction. We use this attribute type of test on high-shrink leather to avoid the use of pressure apparatus or glycerine baths.

A measurement of the shrinkage temperature of each specimen within a sample, or testing by variables, is more informative than an attribute test. It is easily performed if shrinkage occurs somewhat below the boiling point of water. Fortunately, our process permits extensive use of this type of test.

As an initial step we obtained an index of efficiency for the indirect determination of chrome in leather by means of shrink temperature determinations. Within our range of interest (190° to 212° F.), a correlation coefficient of +0.93 was found between shrink temperature and chrome content. Thus, it seems that the historical determination is mathematically justified. So far, other correlation coefficients we have encountered in the tanning industry have been 0.6 or less.

Our next step was to accumulate a large number of random shrink temperature measurements of regular production lots. At the same time lots were identified for future evaluation at finished leather sorting. From this background data it was decided that, for our process, the most satisfactory shrink temperature was 202° F. and that 3° F. made a just noticeable difference to an experienced leather sorter. Our objective specification then became "not less than 95% of the leather shall shrink at 202 ± 3° F." This means that the total variation, as measured by the standard deviation, both between and within lots, must be 1.5° F. or less. These specifications were set some eight years ago. Since then both accidental and intentional deviations from these standards have strengthened our confidence in them. For our process they have stood the test of considerable time; we do not mean to infer that they are absolute values or are necessarily applicable to other plants or other processes.

Needless to say, the setting of objectives is easy; the attainment may be quite difficult. We have not attained our objective but feel that considerable progress has been made.

When systematic testing was first introduced, and without any process changes, we found that only about 60% of our leather would meet specifications. Our most recent survey shows a sustained run with a truncated distribution of 8 to 10% under and 1 to 2% over specifications. As long as we cannot completely meet specification, we are somewhat tolerant of undertannage but not overtannage, since slightly firm leather can be modified at staking.

As experience was gained, needed process modifications, as indicated by shrink temperature determinations, were introduced with increasing confidence. The first modification was simply in drumming time. With a wide between-lot variation, definitely out of limits, it was decided to shorten the drumming time so that now none, or practically none, of the samples of 5 specimens per lot averages over 205° F. Then those lots averaging less than 199° F. are given additional drumming time until on retesting they meet specifications. This procedure explains the truncated distribution mentioned above. Initially, over 40% of the lots required additional drumming; currently, about 10%.

A minor modification in procedure is practiced on weekends or holidays. The stock is tested at the normal time—extra drumming and retesting is done if necessary—and cold water is then added. The temperature and concentration drop "short-stops" the tannage so that the stock can remain in the drum a day or two without overtanning.

We have been able to substantially reduce the within-lot variation. Initially, we had a within-lot standard deviation as high as 3° F. This was considerably greater than our target value of 1.5° F. total, for both between- and within-lots. It meant that, with all other sources of error eliminated, we should expect, at best, not more than 68% of the leather to be within limits. This standard deviation has now been reduced to a little under 1.0° F. Therefore, we should now expect over 99% of the leather to meet specifications if a true lot average of 202° F. could be attained. We believe that a wide within-lot variation is caused by improper balance between rates of chrome fixation and penetration. Empirically we have found the factors that increase within-lot variations to be: low pickle acid, slow chrome feeding, increasing the basicity of the chrome salt, adding less chrome, adding alkali sooner, and shortening the drumming time.

The reduction of between-lot variation is more complex than the reduction of within-lot differences. Almost every factor in the process prior to tanning has shown a statistically significant correlation coefficient, all of low order, usually only 0.2 or 0.3. A few multiple correlation calculations have also been made. To date no use has been made of these calculations. The possibility of interactions is recognized but has been only superficially investigated.

Our largest single source of error between lots seems to be the acid content of the pickled stock. In an early experience we encountered a bimodal distribution of shrink temperature. This type of distribution is well known to statisticians but very disconcerting to beginners. Eventually we found that this distribution was brought about by two pickling procedures, varying in time only and assumed to produce the same result. Actually the shorter time process averaged 10 pounds less acid take-up per 5,000 pound lot and 4° F. higher in shrink temperature. From this we estimate that we should

like to have 95% of our pickle lots entering tan with not more than a plus or minus 7½ pounds acid variation. We have approached this figure by increasing the acid used in pickling. The stock entering tan now carries about 4.7% sulfuric acid on a hide substance basis with a coefficient of variation of 4%. In contrast, stock pickled to contain only 3.6% acid showed a 15% coefficient of variation. Also, simply going from a low to a higher pickle reduced the within-lot standard deviation of the shrink temperature from 3.0° to 1.6° F. The higher amount of acid is at, or near, such a level that the amount absorbed is little affected by any reasonable difference between the amount required and the amount added. We believe that in our process the white weight is a poor index of either hide substance or lime content, making uniform pickling at low levels very difficult. In the absence of a quick quantitative test for either lime, hide substance, or pickle acid, we make use of the automatic control feature of a relatively high pickle.

At low pickle levels any changes in processes such as liming, washing, or bating which will reduce or increase the acid absorbed from a given pickling procedure, will either increase or reduce the shrink temperature in the anticipated direction.

Our experience with formate tannage has been limited, but it does indicate that more uniform results can be expected if it is compared with those obtained with low-level sulfuric acid pickled stock. In addition to its buffering effect and higher pH value formic acid has less affinity than sulfuric acid, in terms of chemical equivalents, for hide substance.

Probably the most valuable contribution of the shrink temperature control program was the recognition of seasonal variations. In winter the direction was undertannage; and in summer, overtannage. This seasonal cycling, a very common occurence, was entirely unanticipated by us. Traditionally fat liquor was increased when going from summer to winter, and the tannage was not suspected at all. We now change the tanning process in three particulars in order to compensate for the seasons. Going from winter extremes to summer extremes, we decrease the float temperature 15° F.; the drumming time, 30%; and the chrome given, 20%. During the transition period the changes are made by small degrees in the order given. Since the introduction of this procedure we have found a substantial reduction in the need for seasonal changes in fat liquor. Also, since recognition of the need for shrink temperature adjustment has less time lag than recognition of the need for fat-liquor adjustment, the quantity of seasonal off-standard leather is reduced.

There are several days each spring and fall, coinciding with abrupt changes in ambient temperature, when the process can be considered completely out of control. Corrective changes are made by trial and error, and considerable hunting is sometimes required. In the near future we plan to make a study of the rate of change in temperature of the drum contents during

tanning. We hope that a time-temperature integration will give us a better basis for processing.

Again we should like to point out that this is only a case history and is not intended to recommend specific objectives for other plants or other processes. However we do agree with an ever increasing number of people that Statistical Quality Control is valuable, both as a working tool and as a way of thinking.

Received November 5, 1957.

Hall's Substitute for Leather. Mix in a suitable vessel 4 parts of wax, 2 of caoutchouc, 1 of resin, 2 of boneblack, and 1 of lampblack, and apply the mixture while warm to cloth or other fabrics by means of a brush. Let it dry thoroughly and repeat the coating several times, allowing the previous coating to become entirely dry before applying the next. This material, after having been lacquered, is principally used for shields for caps.
—*The Techno-Chemical Receipt Book*, ed. William T. Brannt and William H. Wahl. Philadelphia: Henry Carey Baird & Co., 1892.

The student should cultivate the habit of reading them [journals]. Of course he cannot read all of the journals that are published even if he has access to them, but he can browse through several, at least reading the articles which appeal to him most . . . To be sure the research chemist spends a large part of his time searching the literature for things that bear directly on his own problem and necessarily so, but he cannot afford so to narrow himself as to see one small segment of chemistry. The man of one idea has not a whole idea for his one idea is incomplete without its relations to other ideas; the zenith is related to the whole horizon. One must read broadly of many things in order to think deeply on one thing. The research chemist must read everything about his own field but he cannot afford to neglect the rest of chemical literature. It is remarkable how much light is thrown upon a problem from distant sources; one can hardly read a piece of investigation of any sort without finding something that suggests an idea about his own problem.
—*Introduction to Organic Research.* E. Emmet Reid. Princeton, N. J.: Van Nostrand Co., Inc., 1924.

The first chemical journal apparently was the *Chemisches Journal* started in 1778; it was later (1784) called *Crell's Chemische Annalen.* The oldest chemical journal which is still being published is the *Annales de chimie*, begun in 1789. It appeared from 1816 to 1914 under the name *Annales de chemie et de physique*, when it was divided into two separate journals, *Annales de chimie* and *Annales de physique.* . . . The first American chemical periodical was the *American Chemist*, which was published from 1870 to 1877 by that venerable pioneer among American chemists, Dr. Charles F. Chandler, and his brother.
—*A Guide to the Literature of Chemistry.* E. J. Crane and Austin M. Patterson. New York: John Wiley & Sons, Inc., 1927.

TANNING STUDIES WITH DIALDEHYDE STARCH*

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ABSTRACT

Dialdehyde starch, a reactive derivative potentially available at low cost by oxidation of starch, has been shown to have tanning action. Studies were made to determine the effect of such factors as degree of oxidation, method of solubilization, time of treatment, and pH of medium on the rates and degree of tannage.

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INTRODUCTION

The tanning action of certain aldehydes, particularly formaldehyde, has been known for some time, and studies have indicated that tanning action is generally limited to the simpler aliphatic aldehydes of low molecular weight (1,2,3). Recent investigations have shown that the reactivity of dialdehydes toward hide substance is not as critically influenced by molecular weight as in the case of the monofunctional aldehydes (4,5,6). This paper is in the nature of a progress report describing our investigations on the tanning action of dialdehyde starch, also referred to as oxystarch, a polyfunctional aldehyde derived from starch by periodate oxidation. Our interest in dialdehyde starch was stimulated by the recent development of an efficient electrolytic process for effecting this oxidation (7,8,9). In this new process the expensive reagent, sodium periodate, is constantly regenerated electrolytically during the reaction, making dialdehyde starch potentially available at low cost.

EXPERIMENTAL

Materials.—The raw stock was pickled calfskin purchased from a local tannery. Dialdehyde starch was supplied by the Northern Utilization Research and Development Division, the dialdehyde content varying from 10 to 98%.

Preliminary tanning studies.—Dialdehyde starch may be dissolved in water either by heat or with alkalies. The tanning properties of solutions prepared by both of these methods were investigated.

*Presented in part at the Fifty-third Annual Meeting of ALCA, Lake Placid, New York, June 2-5, 1957.
†A laboratory of the Eastern Utilization Research and Development Division, Agricultural Research Service, United States Department of Agriculture.

Method A.—The dialdehyde starch was dissolved by autoclaving a 10% suspension in water at 120° C. for ½ hr. The cooled solution was then adjusted to a concentration of 5% with respect to dialdehyde starch and 10% in sodium sulfate. The pH value of these solutions when used for tanning was maintained in the regions of approximately 5, 8, and 10 by the use of acetate, bicarbonate, and mixed bicarbonate–magnesium oxide buffers respectively. Small pieces of drained pickled calfskin, 4″ x 6″ in size and about 40 g. in weight, were added to 120 g. of the dialdehyde starch solution (3:1 float) in bottles which were gently agitated by rolling on a jar mill. Small portions of these specimens were removed after 2, 6, and 24 hr. for determination of shrinkage temperature and leather-like drying after washing for one day. These data are summarized in Table I.

TABLE I

TANNING OF CALFSKIN WITH DIALDEHYDE STARCH (AUTOCLAVED)*

Expt. No.	Treatment: Dialdehyde Content, %†	Buffer	pH‡	Shrinkage Temp., °C., After: 2 hr.	6 hr.	24 hr.	72 hr.	Neut.**	Leather-like Drying After††
1	95 to 98	HOAc + NaOAc	4.9–5.0	61	72	76	78	—	24 hr.
2	"	0.3*M* $NaHCO_3$	7.3–8.2	74	80	81	83	82	6 "
3	"	1% MgO	9.6–9.5	55	61	79	83	79	24 "
4	"	MgO + $NaHCO_3$	9.4–8.9	69	85	86	87	86	6 "
5	71	HOAc + NaOAc	4.9–5.0	—	66	70	74	—	24 hr.
6	"	0.3*M* $NaHCO_3$	7.3–7.8	68	74	81	82	80	6 "
7	"	1% MgO	10.1–10.2	53	63	73	74	70	72 "
8	"	MgO + $NaHCO_3$	10.0–9.8	68	80	83	79	77	6 "
9	60	HOAc + NaOAc	5.0	—	66	68	72	—	24 "
10	"	0.3*M* $NaHCO_3$	7.2–7.7	67	72	78	81	79	6 "
11	"	1% MgO	10.2	55	62	69	74	72	72 "
12	"	MgO + $NaHCO_3$	9.6–9.4	73	80	83	84	79	2 "
13	29	HOAc + NaOAc	5.0	—	61	62	64	—	>72 "
14	"	0.3*M* $NaHCO_3$	7.1–8.6	63	66	74	82	78	24 "
15	"	1% MgO	10.6–10.4	56	61	68	68	63	>72 "
16	"	MgO + $NaHCO_3$	10.6–10.3	72	73	77	76	73	2 "
17	10	HOAc + NaOAc	5.0	—	60	60	62	—	>72 "
18	"	0.3*M* $NaHCO_3$	7.4–8.8	62	61	68	77	73	72 "
19	"	1% MgO	10.6–10.2	53	53	64	63	62	>72 "
20	"	MgO + $NaHCO_3$	10.6–9.9	68	67	69	72	65	>72 "

*Tanning solution: 5% solution concentration with respect to dialdehyde starch (solubilized in autoclave); 10% in Na_2SO_4.
†Extent of anhydroglucose units of starch converted to dialdehyde structure.
‡At beginning and end of tannage.
**Sample tanned for 3 days then neutralized in acetate buffer (pH approx. 5) for 2 hr.
††Time of tanning which produced specimen showing leather-like drying.

Method B.—A 10% solution of sodium sulfate in water was prepared and sufficient sodium bicarbonate or magnesium oxide (or mixtures of these two

alkaline agents) added to make the solutions 0.3*M* in $NaHCO_3$ and/or 1% MgO. To 120 g. of such a solution was added 6 g. of solid dialdehyde starch and one piece (4" x 6") of drained pickled calfskin. Agitation was provided by carrying out the treatment in bottles rolled on a jar mill. The dialdehyde starch gradually dissolved during the earlier stages of the treatment. The results are tabulated in Table II.

TABLE II

TANNING OF CALFSKIN WITH DIALDEHYDE STARCH (DRY)*

Expt. No.	Treatment: Dialdehyde Content, %†	Buffer	pH‡	Shrinkage Temp., °C., After: 2 hr.	6 hr.	24 hr.	72 hr.	Neut.**	Leather-like Drying After††
1	98	0.3*M* $NaHCO_3$	7.5–8.2	64	73	81	83	83	24 hr.
2	"	MgO, 1%	9.5–9.4	53	66	81	84	80	24 "
3	"	MgO + $NaHCO_3$	9.5–8.8	80	83	86	87	85	2 "
4	71	$NaHCO_3$	7.4–7.8	63	70	80	82	80	24 "
5	"	MgO	10.3–10.2	59	63	71	75	74	72 "
6	"	MgO + $NaHCO_3$	10.8–8.8	74	77	82	83	79	2 "
7	60	$NaHCO_3$	7.3–8.0	62	78	81	84	83	6 "
8	"	MgO	9.5–9.6	57	60	73	77	74	24 "
9	"	MgO + $NaHCO_3$	9.3–9.0	76	78	87	85	86	2 "
10	29	$NaHCO_3$	7.4–8.6	67	71	79	85	83	24 "
11	"	MgO	9.6–9.8	63	63	66	69	70	72 "
12	"	Mg + $HaHCO_3$	9.4	74	82	86	83	79	6 "
13	10	$NaHCO_3$	7.3–8.9	64	66	74	80	78	24 "
14	"	MgO	9.7–9.9	55	62	65	66	64	72 "
15	"	MgO + $NaHCO_3$	10.3–9.8	66	72	70	70	67	6 "

*Tanning solution: 5% on solution basis with respect to dialdehyde starch (added dry); 10% in Na_2SO_4. For other footnotes, see Table I.

Tanning full calfskins.—Into a drum (16½" wide and 5' inside diameter) 10.6 l. of water, 1.38 kg. of Na_2SO_4, and 0.17 kg. of $NaHCO_3$ were charged and dissolved. Two drained pickled calfskins, amounting to 5.3 kg., were added to the drum, which was then run for 1 hr. At the end of this time the pH was 7.4, and an additional 0.23 kg. of $NaHCO_3$ was added followed by 0.53 kg. of solid dialdehyde starch of 95% dialdehyde content. Drumming was continued for 7 hr. After resting overnight (16 hr.) the contents were drummed for an additional 2 hr. At the end of this time the solution, which had an amber color, showed a pH of 8.3, and the T_s of the leather was 79° C. (T_s of a specimen after 7 hr. of tanning was only 66° C.) The contents of the drum were then acidified by adding a total of 0.12 kg. of 80% formic acid in four feeds with 1 hr. of drumming after each feed. The drum rested overnight (pH of the liquor was 4.4), then the tanned skins were washed for 3 hr. The dialdehyde starch–tanned calf-

TABLE III

EFFECT OF pH AND DEGREE OF OXIDATION ON THE FIXATION OF DIALDEHYDE STARCHES BY CALFSKIN

Expt. No.	Tannage*	pH	Ts,°C.	Analysis, % (MFB)				Fixed Aldehyde	
				Total N	Fat	Ash	Hide Subs. N×5.62	% by wt.†	% of H.S.
1	Dialdehyde starch, 95% oxid., autoclaved	6.9	80	16.08	0.38	1.23	90.37	8.0	8.9
2	" " 60% " "	7.0	78	16.52	0.37	0.89	92.84	5.9	6.4
3	" " 44% " "	7.1	74	16.82	0.18	0.73	94.53	4.6	4.9
4	" " 95% " "	9.6	84	16.42	0.30	1.55	92.28	5.9	6.4
5	" " 60% " "	9.7	83	16.61	0.24	1.76	93.35	4.7	5.0
6	" " 44% " "	9.9	79	17.06	0.20	1.33	95.88	2.6	2.8
7	Dialdehyde starch, 95% oxid., dry	7.0	82	16.07	0.23	1.16	90.31	8.3	9.2
8	" " 60% " "	7.2	78	16.30	0.19	1.06	91.61	7.1	7.8
9	" " 44% " "	7.5	77	17.11	0.11	0.77	96.16	3.0	3.1
10	" " 95% " "	9.5	82	16.66	0.27	1.56	93.63	4.5	4.8
11	" " 60% " "	9.7	85	16.40	0.20	2.01	92.17	5.6	6.1
12	" " 44% " "	10.1	80	16.92	0.20	1.76	95.09	3.0	3.2
13	Glyoxal	6.7	80	17.48	0.12	1.18	98.24	0.5	0.5
14	"	9.1	88	17.16	0.24	1.63	96.44	1.7	1.8
15	Untanned, acetone-dehydrated		60	18.05	0.23	0.85	101.44	(−2.5)	

*Concentrations of tanning solutions: 5% for dialdehyde starch, 1.8% for glyoxal; all 10% in Na_2SO_4.
Floats: 2:1, 3:1, 4:1 for dialdehyde starch of 95, 60, and 44% oxidation respectively; 2:1 for glyoxal.
$NaHCO_3$ was used for pH approx. 7; $NaHCO_3$ + MgO for pH approx. 10. Treatment carried out for 24 hr.
†Calculated from balance on MFB; i.e., 100 minus (hide substance + fat + ash).

skin was smooth-grained and showed a shrinkage temperature of 79° C. A sample without fatliquor, dried at room temperature, was almost white and showed good leather characteristics.

This tannage was also carried out at a higher pH (9 to 10) by substantially the same process as described above except that a mixture of magnesium oxide and sodium bicarbonate was used instead of sodium bicarbonate alone (0.14 kg. of MgO in addition to the $NaHCO_3$, prior to the addition of the solid dialdehyde starch in the example above). Tanning at this higher pH was more rapid (T_s after 4 hr. was 83° C.), the leather was tan in color, and the T_s of the 24-hr. specimen was 86° C. (lowered to 82° C. after acidification).

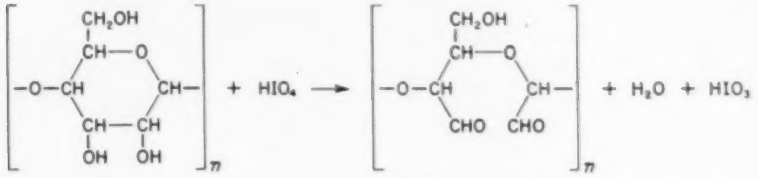
Fixation of dialdehyde starch.—For purposes of analysis pickled calfskin was depickled in sodium acetate–acetic acid buffer, washed, and then dehydrated in several changes of acetone. Pieces of the acetone-dehydrated skin, amounting to about 65 g., were wet back in water for 6 hr., wrung (wrung weight 165 g.), and then tanned for one day with various dialdehyde starches under different conditions as indicated in Table III. After tanning, the leather was washed for one day, air-dried, and ground in a Wiley mill. Moisture, fat, and ash were determined by standard methods (10) and total nitrogen by the semimicro method (11). Fixed aldehyde was calculated as the difference between 100 and the sum of hide substance, fat, and ash on a moisture-free basis. The results are summarized in Table III.

For purposes of comparison, lots of the calfskin (165 g. on wet-wrung basis) were tanned with commercial glyoxal under conditions comparable to the tannage with dialdehyde starch. The tanning solution (312 ml.) contained 18.5 ml. of commercial glyoxal solution of 30% concentration, 33 g. of anhydrous sodium sulfate, and 5.5 g. of sodium bicarbonate. The treatment was carried out for one day, and the pH was 6.7. Tannage with glyoxal at pH 9.1 was carried out by the same procedure except that 3.3 g. of magnesium oxide were used in addition to the sodium bicarbonate. The concentration of glyoxal in the tanning solutions was about 1.8%, in comparison with about 5% for the dialdehyde starch, in order to compensate for the lower molecular weight of glyoxal. The washed, air-dried pieces were then analyzed, and the data included in Table III.

DISCUSSION

Dialdehyde starch is a polymeric aldehyde derivative formed by the oxidation of starch with periodic acid. Periodic acid oxidation offers a specific means for cleavage of α-glycols and has been advantageously used by organic chemists to elucidate the structure of polyhydric alcohols, e.g., starch itself. The following equation illustrates the reaction as applied to starch. In this

oxidation glucose residues of starch are oxidized to a dialdehyde structure as shown below.



Starch Dialdehyde starch

The extent of oxidation can be readily controlled, and a complete range of aldehyde derivatives of starch is made available as the oxidation level varies between 0 and 100%. At 100% oxidation each glucose residue is converted to the dialdehyde structure; at 50% oxidation half of the glucose residues are so altered. Dialdehyde starch is thus an open chain polymer containing aldehyde groups and, if no other bond rupture occurs, should have a molecular weight comparable to the starch from which it is made.

The data in Tables I and II demonstrate the tanning action of dialdehyde starch. Comparable results were obtained whether the dialdehyde starch was first dissolved by autoclaving at 120°C. for ½ hr. or added as the solid directly to the alkaline solutions in which tanning was effected. With the latter procedure a somewhat higher shrinkage temperature was obtained, particularly with the dialdehyde starch of lower oxidation levels. Tanning with the solid dialdehyde starch at pH 7 to 8 was slower than with the autoclaved, probably because the solid material dissolved slowly at this pH. In the drum tannage this was advantageous since it provided an automatic means for the gradual increase of aldehyde concentration in the tanning solution and facilitated the production of a smooth-grained leather.

The data of Tables I and II show that tanning action was not limited to the derivative in which substantially all the anhydroglucose units of the starch were oxidized to the dialdehyde structure. At pH of 7 to 8 practically the same maximum shrinkage temperature (T_s about 80°C.) was eventually attained with the starches ranging from 98 down to 29% in dialdehyde content; however, the rate of tanning decreased with decreasing dialdehyde content. The tanning action of starch of 10% dialdehyde content was extremely poor as indicated not only by the lower T_s but also by the appearance of the treated specimens.

An interesting feature of the data in Tables I and II is the comparison of the magnesium oxide system with a mixture of this oxide and sodium bicarbonate to control the pH. Even though the pH values of these two systems were substantially the same, the latter system resulted in a much more rapid tanning action and was preferable to the former.

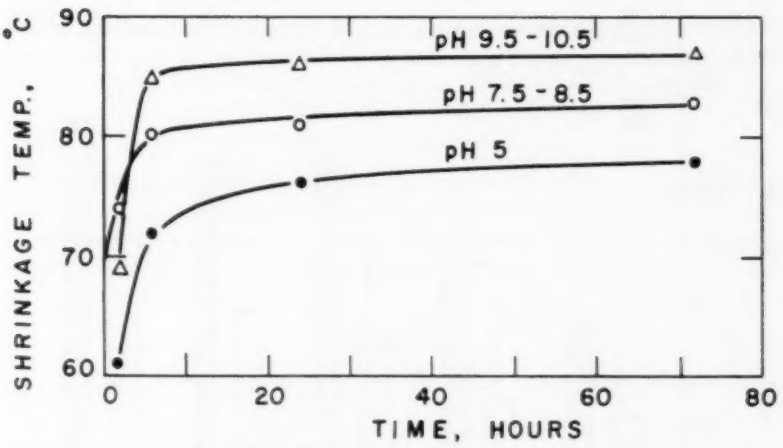


FIGURE 1.—Rate of increase in shrinkage temperature in tanning calfskin with autoclaved dialdehyde starch (95% dialdehyde content).

Figure 1 shows the rate of increase of shrinkage temperature upon tanning calfskin with the autoclaved dialdehyde starch of 95% dialdehyde content. In common with other aldehydes the rate of tanning increased with increasing pH. The maximum Ts also increased with pH and was essentially reached in 6 hr. in alkaline solutions and in 24 hr. in slightly acidic medium. In general, shrinkage temperatures of approximately 78°, 81°, and 86° C. were attained in 24 hr. at pH of about 5, 8, and 10 respectively.

Correlation of the shrinkage temperature after 24 hours of treatment (autoclaved dialdehyde starch) with extent of oxidation of the starch is shown in Figure 2. At pH 5 there is a marked lowering of the 24 hr. Ts with decreasing extent of oxidation. In alkaline solutions the lowering of Ts is not so pronounced until the extent of oxidation falls below 60%. As can be seen from Figure 1, the tanning action of the dialdehyde starch of 10% dialdehyde content was considered poor when used under the conditions of our experiments. In general more favorable leather characteristics were obtained as the dialdehyde content of the starch increased, and from our studies thus far the dialdehyde starch that is almost completely oxidized to the dialdehyde structure seems to be the most suitable material as regards tanning action.

The fixation of aldehyde and comparison with the simplest dialdehyde, glyoxal, were of interest in this study. Methods for the direct determination of these aldehydes are not presently available, hence the fixed aldehydes were determined by difference. The data in Table III show a decreasing fixation of aldehyde with decreasing dialdehyde content of the dialdehyde starch. Perhaps the explanation lies in the fact that although the dialdehyde

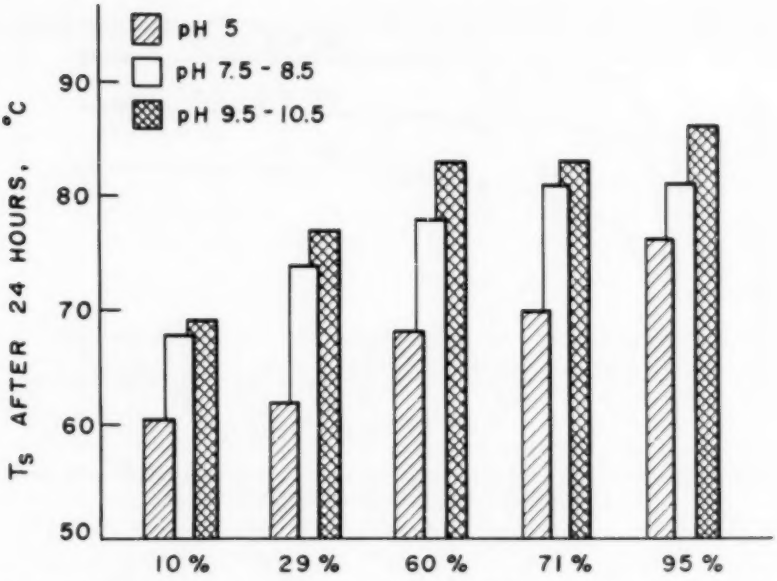


FIGURE 2.—Shrinkage temperature of calfskin treated 24 hr. with autoclaved dialdehyde starch of different degrees of oxidation at 3 pH levels.

starch solutions were all comparable on a solids basis (5% by weight), they are not comparable in concentration on an equivalent aldehyde basis. In contrast to glyoxal, fixation of dialdehyde starch was less at pH 10 than at pH 7, and this may indicate that less dialdehyde starch is needed in tanning at the higher pH. Of interest is the fact that at pH 7 fixation of dialdehyde starch was considerably higher than fixation of glyoxal. However, the fixation was not as high as expected from a derivative of a substance of such high molecular weight as starch, and it appears probable that depolymerization of the dialdehyde starch molecule is a complicating factor in this reaction.

Preliminary experiments have indicated that dialdehyde starch–tanned leather can be retanned with conventional mineral and vegetable tanning agents.

SUMMARY

Dialdehyde starch has been shown to have tanning action. The tanning action varied with the extent of oxidation of the starch. The reactivity and fixation decreased with decreasing level of oxidation, and in general the most promising leathers were obtained using dialdehyde starch of high aldehyde content. In common with other aldehydes, tanning with dialdehyde starch

in the acid range was slower than in the alkaline region. Tanning of calfskin was complete in a period of 6 to 24 hr. and the shrinkage temperature of the leather was 80° and 86° C. when tanned at pH 8 and 10 respectively.

ACKNOWLEDGMENT

The authors wish to express their gratitude to W. Windus for suggestions and constructive criticism, and to staff members of the Northern Utilization Research and Development Division, United States Department of Agriculture, Peoria, Illinois, for supplying the samples of the dialdehyde starch used in this investigation.

REFERENCES

1. Gustavson, K. H. *The Chemistry of Tanning Processes* (New York: Academic Press, Inc., 1956) pp. 244, 278.
2. ———. *J. Intern. Soc. Leather Trades' Chemists*, **24**, 377 (1940).
3. ———. *Svensk. Kem. Tid.*, **59**, 98 (1947).
4. ———. *Ibid.*, **61**, 114 (1949).
5. Seligsberger, L., and Sadlier, C. *JALCA*, **52**, 2 (1957).
6. Fein, M. L., and Filachione, E. M. *JALCA*, **52**, 17 (1957).
7. Dvonch, W., and Mehltretter, C. L. *J. Am. Chem. Soc.*, **74**, 5522 (1952); U. S. Pat. 2,648,629, August 11, 1953.
8. Mehltretter, C. L., Rankin, J. C., and Watson, P. R. *Ind. Eng. Chem.*, **49**, 350 (1957).
9. ———. U. S. Pat. 2,713,553, July 15, 1955.
10. ALCA Provisional Methods, May 1954.
11. Willits, C. O., and Ogg, C. L. *J. Assoc. Offic. Agr. Chemists*, **33**, 179 (1950).

Received October 31, 1957.

DISCUSSION

Dr. Lollar (Tanners' Council Laboratory, University of Cincinnati): I wish to express my own and, I am certain, your thanks, to Dr. Filachione for his very interesting paper evaluating this relatively new material which certainly seems to have some potentialities for our industry.

Although the material was referred to as a dialdehyde starch, I wonder if we should not consider the fact that it is really a polyfunctional material, since because of its molecular weight, there are more than two aldehyde groups per molecule. This might explain its potential tanning function. I can indicate to you from our studies on the use of dialdehyde starch as a reactive aldehyde on keratins that it is truly a material with considerable aldehyde functionality and potential value as a modifying agent for proteins.

I think that the leather will speak for itself, and I trust that you will take an opportunity to look at it.

I was particularly interested in the success achieved with the dry addition of the material. In our work with the material on keratin we have found that

the dissolving of the material is one of the limitations of its use from a practical standpoint. The fact that it works by adding the dry material would be of considerable advantage in the practical application of this material in the tannery.

BORIS MONSAROFF (Hamilton, Ontario): It seems to me that in other carbohydrates such as cellulose there is the possibility of application here. Did you ever try out oxycellulose?

DR. FILACHIONE: No, we have not. The term oxycellulose may be applied to various types of oxidized cellulose. We would be interested in a periodate oxidized cellulose but we know of no one who has it available.

MR. MONSAROFF: Dr. Purvis of Montreal has done work on the periodate oxidation of cellulose rather than starch. I would like to find out if other carbohydrates such as cellulose would have potential application.

DR. FILACHIONE: The periodate oxidized cellulose would be similar to periodate oxidized starch. It should have the same possibilities.

MR. MONSAROFF: You have not tried it?

DR. FILACHIONE: No.

MR. LOTZ (Albert Trostel & Sons Co.): In treating your calfskin squares you started from pickled stock and then depickled. Would you have gotten an improvement in your leather if you had skipped the pickling step entirely and started from the high pH of the bating step?

DR. FILACHIONE: We have not carried out experiments starting with the bated stock. We used the pickled stock because it was convenient to purchase and store it in that state.

MR. LOTZ: It might be interesting to skip the pickling entirely and start with bated stock, thus starting at pH 8 to 9.5, which fits the region in which you are working.

DR. FILACHIONE: It would be interesting to try.

DR. LOLLAR: The drum depickling operation is a tricky operation and you certainly would hesitate to try to do something like that from a practical standpoint if you did not have to.

DR. FILACHIONE: We have carried out the treatment using the pickled stock and just adding the bicarbonate in excess of the amount required for depickling, and then adding the dialdehyde starch. So we don't have to wait actually for a depickling operation. We can carry it out all in one step.

DR. LOLLAR: In that regard, I wonder if you have any indication that there is any reaction, even at more acid pH values than those you reported here? In our keratin work we have found evidence of reaction between the oxystarch and protein at a pH as low as 3.

DR. FILACHIONE: No, we have not gone to very low pH's. I think our lowest pH was in the neighborhood of 3.6, which is the pH of the autoclaved dialdehyde starch.

JEROME J. RITTER (Rohm & Haas Co.): Did you try any of these experiments at higher temperatures in the tanning? And also, does this product have any of the odor drawbacks that regular formaldehyde does?

DR. FILACHIONE: No, we have not tried this at other than room temperature. With regard to odor, there is hardly any odor at all. There is a very slight odor, but nothing that is objectionable or irritating.

MR. RITTER: Would you classify the leather as comparable to straight formaldehyde leather?

DR. FILACHIONE: Oxystarch is similar to formaldehyde in that we have an aldehyde tannage. The leathers are comparable in stability on the alkaline side. However, oxystarch gives a considerably higher fixed aldehyde content than does formaldehyde, and the former produces a fuller leather.

DR. J. H. HIGHBERGER (United Shoe Machinery Corp.): Do you have quantitative data about the amounts of starch fixed?

DR. FILACHIONE: Yes, we have. The leathers were analyzed for total nitrogen, fat, and ash, and fixed aldehyde was calculated by difference. Fixed aldehyde was about 8% on an analytical basis.

DR. HIGHBERGER: Is that the maximum?

DR. FILACHIONE: Our highest was 8.3%. It is interesting that the weight gain, based on conditioned samples, was about 11%.

ADOLF SCHUBERT: Is the material being produced at the present time?

DR. FILACHIONE: As far as I know, it is not being produced commercially at the present time. Our samples were supplied by the Northern Utilization Research and Development Division, U. S. Dept. of Agriculture, Peoria, Ill. They developed the new electrolytic process for the preparation of this material and probably are able to supply small samples.

DR. LUDWIG SELIGSBERGER (Quartermaster Research and Engineering Center): I would like to caution against using higher temperatures, particularly at higher pH values. I think Dr. Filachione may also have found

that the material is not too stable at a pH of around 8.5 or 10 and disappears in solution gradually when used for tanning. I would say for this reason that maybe it would be advisable to add it in several feeds and not to add the dry material all at once.

DR. FILACHIONE: Thank you. That is interesting.

JAMES KELLY (Ellithorp Tanning Co.): Was there any special procedure used in tanning these sample skins?

DR. FILACHIONE: This was tanned in our laboratory and then processed through a tannery with a regular pack.

MR. KELLY: Were the skins treated with sulfonated oil or cationics?

DR. FILACHIONE: I have no specific information with regard to the fat liquor.

DR. LOLLAR: As far as you know, no modification was made of the process customarily used in that calfskin tannery?

DR. FILACHIONE: That is correct.

C. DAVID WILSON (Fred Rueping Leather Company): What would you expect the color of this leather to be, had it not been dyed?

DR. FILACHIONE: Tanning at pH 8 gave a somewhat off-white leather, while tanning at pH 10 produced a tan-colored leather.

CHARLES W. MANN (Quartermaster Research and Engineering Center): Dr. Filachione was kind enough to let us have a sample of his material to use in connection with our research. We were conducting a series of tests on heavy leather, attempting to make sole leather by first tanning with aldehyde and after stablilizing the fiber in this manner, adding filling materials. We made a tannage with dialdehyde starch, and under conditions where we used about 1.5 to 2 normal carbonate solutions and then reacidified to a pH of 5, we got overnight tannage that was very satisfactory. We had no difficulty whatever except, as Dr. Seligsberger pointed out, we did add material in several feeds. But the tannage was satisfactory. The leather had a very good color and compared favorably with the other leathers we had.

After we filled it with conventional vegetable tanning materials, adding weight and solidity to it, it was rated very satisfactory by the tanners as compared with ordinary sole-type leather. Dr. Filachione has a sample of that leather, and I think he will agree it is good quality.

DR. FILACHIONE: Yes. I might point out that this dialdehyde starch is quite sensitive to alkali. We tried to run the pH up beyond 10 by using lime,

but the pH came down to 6 or 7. We were unable to maintain the pH at about 12.

H. A. TETREAULT (A. C. Lawrence Leather Co.): Did you find that this material was extremely hygroscopic?

DR. FILACHIONE: Yes, this leather does absorb water quite rapidly.

WILLIAM J. MCDERMOTT (Rohm & Haas Co.): At your higher pH values do you find that you get further oxidation of the aldehyde, especially in the presence of the alkaline earth metals such as calcium or magnesium, which might account for your change in color going more toward the brownish?

DR. FILACHIONE: We really don't know.

MR. MCDERMOTT: I wondered if some of the aldehyde group went further than the carboxyl, or whether you get some form of condensation as in the case of formaldehyde.

DR. FILACHIONE: There is some question about what happens to dialdehyde starch in alkaline solutions, and the chemistry involved is largely unknown.

MR. MCDERMOTT: Have you done anything on retannages?

DR. FILACHIONE: Yes, we have carried out preliminary experiments on combination tannages, mainly retannage with chrome, alum, and vegetable tannins. It seems to be straightforward and comparable to other aldehyde tannages as regards combination tannages.

JOSEPH N. ORIETAS (Albert Trostel & Sons Co.): I wonder if you have run any aging tests on the finished leather, and how such a leather would behave during storage?

DR. FILACHIONE: No, we have not. We have heated some of this leather in an oven at 90° to 100°C. for a period of a day, and the shrinking temperature goes down under these conditions.

DR. LOLLAR: From a chemical standpoint it has been our observation that the reaction between the dialdehyde starch and the protein yields a product rather typical of the other aldehyde tannages. I would expect, as a first approximation, that this might function very similarly to formaldehyde—maybe a little more like glyoxal—from a chemical standpoint.

DR. FILACHIONE: From the standpoint of response to ultraviolet light, leather tanned with dialdehyde starch behaved similarly to glyoxal-tanned leather, that is, both were bleached.

THE ACTION OF ACRYLONITRILE AND ACRYLAMIDE UPON COLLAGEN

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ABSTRACT

Acrylonitrile and acrylamide are shown to react with limed hide in strongly alkaline solutions. The fixation of the monomers under such conditions results in a lowering of the shrinkage temperature and in a decreased chrome fixation. The dry fiber strength of the resulting leather is not materially affected. The ε-amino groups are considered to be the active sites in the cyano- and carbamoylethylation of collagen.

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INTRODUCTION

In caustic solutions cellulosic materials can be cyanoethylated without difficulty. Proteins lack the necessary resistance toward strong alkalies and cannot be treated in the same manner. Recently, however, wool has been cyanoethylated under relatively mild conditions (1). The wool was first soaked at room temperature in a solution of 4 g/l or less NaOH and then treated with a large excess of acrylonitrile at 60°C. In the cyanoethylation of cotton the reaction temperatures usually range from 65° to 85°C. A recent pilot-plant experiment (2) demonstrated that the nitrogen content of yarn after cyanoethylation at less than 40°C. is not significantly lower than after a similar treatment at the usual temperatures. This re-evaluation of the role temperature plays in cyanoethylation processes seems to the authors to open up possibilities of reacting acrylonitrile with collagen.

Acrylonitrile is unstable in alkaline solutions. In the presence of water it converts mostly into β,β′-oxydipropionitrile (bis-2-cyanoethylether), $O(CH_2\text{-}CH_2\text{-}CN)_2$, in part into acrylamide, $CH_2\text{-}CH\text{-}CONH_2$, and also into sodium acrylate (2). Only acrylamide, which is now available as a pure crystalline product, is still capable of reacting with cellulosic materials. Acryla-

mide combines with cotton at 50°C. in precisely the same ratio of 1 mole for 5.7 anhydroglucose units which prevailed in the cyanoethylation of yarn below 40°C. (3). It may be assumed, therefore, that both acrylonitrile and acrylamide can be introduced with equal ease into the collagen molecule. How attempts to prove this succeeded is described in the present paper.

New modifications of collagen may prove to be feasible for extending its usefulness as in the case of other materials. In the case of cotton, for example, cyanoethylation has been found effective in improving its dyeability and increasing its rot resistance. The present study, exploratory as it necessarily is, may point the way toward similar improvements. Such a possibility is suggested by the observation that the formaldehyde fixation can be increased by the reaction with acrylamide.

EXPERIMENTAL

Techniques similar to those employed in a recent study on aldehydes (4) were used to overcome the swelling effect of alkaline solutions upon collagen. Either a so-called alkaline pickle was employed, i.e., the Na_2SO_4/NaOH system which alone leaves hide flaccid at pH values beyond 11, or NaOH was added to 2*N* Na_2CO_3 solutions which also have no plumping action. The Na_2CO_3/NaOH system does not cause the hides to become as flaccid as in the Na_2SO_4/NaOH system. A few experiments were conducted in the absence of caustic soda in order to investigate the reactivity of acrylonitrile or acrylamide at lower pH values.

For most experiments pickled cow grains were used. Only the first experiment was conducted with pickled steer bends. Pieces weighing 50 to 350 g., selected from opposite locations on two sides of a single hide, were tumbled sufficiently long to assure equilibrium with the alkaline solutions before introducing the monomers. In their presence agitation continued 2 hr. for the cow grains and 5 hr. for the steer bends.

Thereafter, in the case of the cow grains, the liquor pH was gradually lowered to approximately 4.5 by the addition of formic acid. At the outset the intervals between feeds of the acid were 10 to 15 minutes; they were lengthened when the pH of the solution approached the desired range. In the Na_2CO_3/NaOH system as much as 15%, on the pickled weight, of 90% formic acid was needed for reaching the desired pH. In the Na_2SO_4/NaOH system between 2.5 and 3% was required.

In the case of the steer bends the liquor was drained off before the first portion of formic acid was added. Only the Na_2CO_3/NaOH system was investigated and because only the alkali inside the hide pieces remained to be neutralized, the acid consumption was 2/3 lower than for the cow grains.

Finally all pieces were washed in running tap water as well as in several changes of distilled water; most were subsequently chrome tanned. Small

strips were air-dried. Only pieces of the steer bend, in the first test, were tanned with formaldehyde by adding 5%, on pickled weight, of a commercial solution directly to the alkaline liquor. Assuming 20% of the pickled pelt to be collagen, this quantity equals 9 parts H_2CO for 100 parts or 3 millimoles per 1 g. collagen. This ratio was selected because it had given yields of about 20% in a recent study (4).

The chrome tannage follows, on the whole, Gustavson's technique (5) which purposely employs a very large excess of chrome in order to measure the maximum capacity of collagen or modified collagen for its fixation.

In Gustavson's experiments a 33% basic chromic sulfate liquor represented the cationic type, while a glucose-reduced liquor containing 2.5 moles Na_2SO_3 per mole chromic oxide served as the example of a chrome liquor containing mostly noncationic chrome. The cationic chrome liquor in our study was a 33% basic commercial chrome tanning material, boiled and aged as a solution containing 100 g/l Cr_2O_3. By using 200 volume % of this solution, the ratio of Cr_2O_3 to pelt was 1 to 1. When the noncationic chrome liquor was prepared according to Gustavson's directions, it jelled while aging. In a second solution a pH of 5.8 was found a few hours after preparation. Therefore 0.13 moles H_2SO_4 per mole Cr_2O_3 were added, which lowered the pH to 3.7; within 2 weeks the pH gradually rose again, this time to 4.6, necessitating once more the addition of 0.065 moles H_2SO_4 per mole Cr_2O_3. On the day when the solution was used its pH was 4.2. Since it contained approximately 20 g/l Cr_2O_3, it was necessary to apply 1000 volume % in order to reach the same ratio for Cr_2O_3 as in the cationic liquor.

The tannage with the cationic liquor took place at pH 3.3 preceded by a mild pickle in an H_2SO_4/NaCl system. During tannage, a total of 0.16 moles soda ash per mole Cr_2O_3 was added in small feeds over a period of 6 hr. to promote the chrome pickup.

The second tannage was not preceded by a pickle nor did it require the addition of soda ash. The milling time, however, was the same as in the first one.

After the tanned hide pieces were kept in the wet stage for 16 hr., they were thoroughly washed and air-dried.

ANALYTICAL METHODS

Physical.—The shrinkage temperatures were determined according to standard techniques except in the case of chrome pieces which were thought to shrink over 100°. These measurements were made with the Transverse Shrinkage Meter (6). Burst measurements were conducted on a Scott Tester with the 1/8-inch plunger (7).

Chemical.—Cyanoethylated products are, as a rule, assayed by the Kjeldahl method. Since they usually are free, or nearly free, of nitrogen

before the cyanoethylation, a direct digestion is, without doubt, the most reliable analytical procedure. In fact, a warning has recently been issued against the practice, apparently wide spread, of omitting the digestion with H_2SO_4 (8): the direct distillation of the NH_3 formed on boiling cyanoethylated cotton with dilute NaOH at best yeilds only 95% of the nitrogen. Methods based on the digestion of acrylonitrile- or acrylamide-treated raw hide would probably be no more precise since the correct distribution of the nitrogen between collagen and monomers could only be found if the balance of all constituents (e.g., ash, grease) as well as the nitrogen factor was accurately known.

The direct distillation, on the other hand, yields excess NH_3 because dilute alkali hydrolyzes collagen (9). After tanning pickled cowhide in the manner described above for maximum chrome pickup, the volatile nitrogen was about 6% of the total nitrogen for the cationic and noncationic tannages alike. These figures were applied as correction values to the results obtained by hydrolyzing in the same manner chrome-tanned modified hide. The distillation was improved by conducting it in an apparatus developed for H_2CO determinations in leather (10). One gram of ground leather was hydrolyzed by boiling it with 100 ml. of a 0.6*N* NaOH solution. After the first 20 ml. were distilled over, the volume was maintained by slowly adding the water needed until 2 fractions of 100 ml. each had been collected and summarily titrated. A third fraction contained no more than 0.05 meq. NH_3 and could, therefore, be dispensed with in the controls as in the treated specimens.

The result of the titration was a direct measure of the quantities of bound acrylonitrile or acrylamide. The acid consumed was also subtracted from the total acid consumption in a standard Kjeldahl determination in order to obtain true hide substance values. The factors for the conversion of nitrogen into acrylonitrile and acrylamide are 3.8 and 5.0 respectively.

Chrome was determined by wet oxidation. The formula of Kanagy (11) was used to arrive at a figure for the chrome complex in both the cationic and the noncationic tannages, although its validity has only been proven for the former tannage.

RESULTS

Treatments.—Substitutions of specific groups do not qualify as tannages since they do not cause cross linking. In fact, many instances are known where they may even effectively block the reaction with selective tanning agents. In these cases significant decreases in shrinkage temperature have been observed. In our experiments with acrylonitrile and acrylamide therefore, observations of the T_s changes were the first indications of a reaction taking place between these monomers and the collagen.

TABLE I

SHRINKAGE RESISTANCE OF STEERHIDE TREATED WITH ACRYLONITRILE OR ACRYLAMIDE WITH OR WITHOUT A FORMALDEHYDE AFTERTREATMENT

(Pickled steer bends, in 50 volume percent† solution of 240 g/l Na_2CO_3 and 50 g/l NaOH)*

	Acrylonitrile	Acrylamide
% monomer†	6	7
Ts, °C., at pH 11.8, 2 hr. later	52	55
pH lowered with formic acid to	5.6	5.7
Ts, °C., after lowering pH and subsequent washing:		
a) for H_2CO-treated pieces	64	72
b) for pieces not treated with H_2CO	50	50

*Pieces paired off as required on the basis of bilateral symmetry.
†On pickled weight.

Table I presents these observations in tests with pieces of steerhide which have been more closely described above. When the treatment with acrylonitrile or acrylamide preceded a formaldehyde tannage, the pieces shrank 28° and 20° C. respectively lower than without it. This statement is based on the recent observation that under comparable conditions a formaldehyde-tanned steerhide shrinks at 92° C. (4), or 29° higher than the same hide untanned*. By comparison the rise after carbamoylethylation was only 22° C. and after cyanoethylation, 14° C.

The next set of experiments had the purpose of ascertaining whether or not NaOH is indispensable for reacting the monomers with collagen. In the cyanoethylation of cotton and wool caustic soda is always used. The new experiment employed either soda ash in the same concentration as the previous one, which was approximately 2*N* after equilibration with the hide pieces, or, as the example of a milder alkali sodium sesquicarbonate for which a final concentration of about 1.5*N* was selected. The quantity of monomers employed was approximately double in order to insure a reaction if one was at all possible under the new conditions. Further details are presented in Table II together with the T*s* values obtained at the same two stages as in Table I. The table shows that the highest pH was 9.8 as against 11.8 in presence of NaOH and that only acrylonitrile is still capable of materially lowering the T*s* of hide under these circumstances. Acrylamide displays a stronger lyotropic effect (12*b*) in the alkaline range than before, simply because its concentration was raised from 0.8 to more than 1.8 moles/l. A piece of hide shrank at 47° C. when removed from the acrylamide Na_2CO_3 solution of pH 9.8, but another piece taken later shrank 18° C. higher when free of electrolytes.

*Gustavson (12*a*) records a slightly higher increase of 32°C.

TABLE II

SHRINKAGE RESISTANCE OF COWHIDE TREATED WITH ACRYLONITRILE OR ACRYLAMIDE IN NONCAUSTIC ALKALINE SOLUTIONS

(*Pickled cow grains, in 50 volume percent* solution*)

	Acrylonitrile		Acrylamide	
% Na_2CO_3*	12.5	—	12.5	—
% $Na_2CO_3 \cdot NaHCO_3 \cdot 2H_2O$*	—	15.0	—	15.0
% monomer*	12.0	12.0	16.0	16.0
pH, 90 minutes later	9.7	9.5	9.8	9.4
pH lowered with formic acid to	4.1	3.8	4.1	3.9
T*s*, °C, before lowering the pH	51	54	47	53
T*s*, °C., after lowering the pH and subsequent washing	53	55	65	58

*On pickled weight.

TABLE III

SHRINKAGE RESISTANCE OF COWHIDE TREATED WITH ACRYLONITRILE OR ACRYLAMIDE IN SWELLING–DEPRESSING CAUSTIC SOLUTIONS

(*Pickled cow grains in 50 volume percent* solution*)

	Acrylonitrile		Acrylamide		Control	
% Na_2CO_3*	12.0	—	12.0	—	12.0	—
% Na_2SO_4*	—	12.5	—	12.5	—	12.5
% NaOH*	3.1	3.0	3.1	3.0	3.1	3.0
% monomer*	12.0	12.0	16.0	16.0	—	—
pH lowered to	5.0	5.1	4.9	4.8	4.1	4.0
% formic acid (90%) added for lowering pH	15.0	2.5	15.0	1.3	9.5	1.6
T*s*, °C., before lowering pH	55	54	43	43	59	63
T*s*, °C., after lowering pH and subsequent washing	49	49	52	52	63	63

*On pickled weight.

An experiment designed for a comparison between the "alkaline pickle" and a solution of caustic alkali in 2*N* soda ash is recorded in Table III. In both instances the quantity of sodium hydroxide was about the same. However, acrylamide, for which this effect was already considerable in the absence of NaOH (Table II), now caused a T*s* depression of 20° as against 16° before.

In the case of acrylonitrile the lyotropic effect is probably caused by secondary products and is much less pronounced, although somewhat higher than in the "Controls" which contain no monomers at all. The permanent T_s losses are 14° C. for the cyanoethylated and 11° C. for the carbamoylethylated hide, regardless of the alkaline bath used. These decreases are not very different from those obtained on much heavier hide with about half of the monomer concentration (Table I). Yet the denser fiber structure of steer bends seemed to obscure the greater T_s depressing effect of acrylonitrile, at least before a retannage was applied, whereas grain splits show the difference without it.

All hide pieces dried out as horny and stiff as raw hide with a brownish color. In the wet stage their color depended less on the monomer than on the alkaline system employed. Still, the modified hide pieces could be distinguished from pickled ones of the same hide which had not been modified. Table IV attempts to describe the color hues observed. Evidently the grain was less prone to color changes than the flesh side.

TABLE IV

COLOR CHARACTERISTICS OF COWHIDE
AFTER TREATMENT WITH ACRYLONITRILE OR ACRYLAMIDE

(In the wet stage after de-alkalizing and rinsing)

	Alkaline System			
	Na_2SO_4/NaOH		Na_2CO_3/NaOH	
	Grain	Flesh	Grain	Flesh
1) Untreated	grayish white	light purple	grayish white	light purple
2) Acrylonitrile-treated	purplish	grayish white	grayish white	dark purple
3) Acrylamide-treated	grayer than (1)	lighter purple than (1)	grayish white	dark purple

Examination of chrome leathers.—Treated pieces and controls of Table III, after being chrome tanned as described above, were tested for thickness, strength, and shrinkage resistance (T_s). The figures obtained for the first two of these properties are compiled in Table V. The T_s values will be presented separately in an attempt to link them with the chrome content. A final tabulation will disclose the finding of the chemical analysis.

Strength properties.—The burst measurements, as recorded in Table V, allow one important conclusion: The strength of the leathers was not affected by reacting the hide with the two monomers before tanning. The only significant difference in strength which can be observed on untreated

TABLE V

THICKNESS AND STRENGTH CHARACTERISTICS OF CHROME-TANNED LEATHER MADE FROM CYANOETHYLATED OR CARBAMOYLETHYLATED COWHIDE

	Acrylonitrile		Acrylamide		Controls	
	Na_2CO_3/NaOH	Na_2SO_4/NaOH	Na_2CO_3/NaOH	Na_2SO_4/NaOH	Na_2CO_3/NaOH	Na_2SO_4/NaOH
Thickness, in.						
Cationic tannage	0.090	0.085	0.092	0.091	0.079	0.096
Noncationic tannage	0.101	0.097	0.094	0.102	0.091	0.094
*Bursting load, lb.**						
Cationic tannage	53	43	50	42	33	38
Noncationic tannage	72	62	65	41	48	61
Bursting strength, lb/in						
Cationic tannage	590	500	550	460	420	400
Noncationic tannage	710	640	690	390	530	640

*Avg. of 8 determinations.

TABLE VI

CHROME CONTENTS AND SHRINKAGE TEMPERATURES OF CHROME-TANNED LEATHER MADE FROM CYANOETHYLATED OR CARBAMOYLETHYLATED COWHIDE

	Acrylonitrile		Acrylamide		Controls	
	Na_2CO_3/NaOH	Na_2SO_4/NaOH	Na_2CO_3/NaOH	Na_2SO_4/NaOH	Na_2CO_3/NaOH	Na_2SO_4/NaOH
Chromic oxide, percent on hide substance basis						
a. Cationic tannage	9.3	8.9	10.3	10.3	11.6	11.6
b. Noncationic tannage	11.1	11.2	14.9	22.1	17.5	16.0
Difference b – a	1.8	2.3	4.6	—	5.9	4.4
Ts, °C. (water only, under pressure)						
a. Cationic tannage	102	102	112	110	118	116
b. Noncationic tannage	96	98	111	109	115	113
Difference a – b	6	4	1	1	3	3
Ts, °C. (glycerin only):						
a. Cationic tannage	111	110	121	120	133	128
b. Noncationic tannage	109	111	121	121	133	135
Difference a – b	2	−1	0	−1	0	−7
Ts, °C., increase in glycerin:						
a. Cationic tannage	9	8	9	10	15	12
b. Noncationic tannage	13	13	10	12	18	22

and treated leather pieces alike is connected with the tannage. The noncationic sulfito-chrome liquor gives stronger leather. This is the more remarkable since this liquor causes more chrome to be fixed (Table VI). The same liquor produces a somewhat fuller leather. The increase in thickness averages about 8% for the whole set of specimens. Consequently the increase in bursting strength is smaller than that in bursting load, namely 20% versus 26%. For the untreated controls the increases are 30% and 35% respectively. These percentages are based on the original measurements, not on the rounded figures of Table V. The alkaline systems also seemed to exert a distinct influence on the strength properties when the test pieces were selected for them on the principle of bilateral symmetry. This was, however, not the case with the controls because of a dearth of specimens. The "alkaline pickle" lowered the bursting load of the leather by about 22%, regardless of the chrome liquor in which it was tanned. The bursting strength was also 15 to 20% lower; here the loss was greater for cationically tanned leather which as a whole turned out to be inferior in strength to the sulfito-chrome-tanned hide pieces.

Visual and tactile inspection.—None of the leathers were fatliquored before being tested. Those tanned with cationic chrome were generally more pliable and less tender on the grain because of their lower chrome content (Table VI). By reacting with the monomers the leather became softer and more flexible; the pieces treated in presence of soda ash felt drier and stiffer, presumably because they retain less natural grease. A pronounced greenish cast was typical of the sulfito-chrome tannage, while the cationic liquors produced the usual bluish-green color.

Relationship of chrome pickup to shrinkage resistance.—In Table VI chrome contents are shown in juxtaposition with shrinkage temperatures obtained in glycerin and in water. In appraising the figures presented in this table one notes the following: (*a*) The alkaline systems employed do not influence chrome fixation or T*s*. (*b*) By a noncationic tannage more chrome is fixed than by a cationic tannage, while the T*s* is slightly lowered. (*c*) After reacting with acrylonitrile hide picks up less chrome than it would normally, but after reacting with acrylamide it fixes either the same amount or even more. However, it is quite possible that the single figure of 22.1% Cr_2O_3, representing the highest fixation in the table, is the combined result of a tannage and an excessive aggregation of the sulfito-chrome complex leading to a high interfibrillary deposition. Gustavson also recorded inordinately high chrome contents in sulfito-chrome leather (14), without, however, considering the possibility of some of the chrome being held by mechanical forces after aggregation has progressed beyond a certain point. (*d*) The T*s* is lowered by the attachment of monomers to the hide substance, more so with acrylonitrile than with acrylamide, and more by a noncationic

than by a cationic tannage. (*e*) In glycerin the T_s is higher than in water as may be expected from data linking it to the medium's dielectric constant (14*b*). The difference is larger for a sulfito-chrome tannage than for a cationic chrome tannage, and considerably larger without a treatment than after acrylamide or acrylonitrile. The T_s values by the ALCA method are not shown in Table VI because the controls did not shrink before the boiling point of the mixture. The cyanoethylated pieces shrank 5°–8° higher and the carbamoylethyled pieces 1°–3° lower than in water under pressure.

Fixation of monomers and chrome complex.—Determination in the leathers listed in Table III of hide substance, chrome complex according to Kanagy (11), and the two monomers, where present, gave the results of Table VII. Since natural grease or inorganic matter other than chrome was not determined, the sum total was not expected to approach 100%. Instead, in most cases, it was even higher than 100. In three instances where it exceeded 102, the figures for the chrome complex were also very high, and the nature of the tannage was noncationic. Under these conditions, apparently, Kanagy's formula is not valid, an observation which seems to confirm the idea expressed above that some chrome has aggregated and is no longer chemically bound to collagen. Table VII also shows that the fixation of acrylonitrile in millimoles/g. collagen is, on the average, about twice as

TABLE VII

CHEMICAL COMPOSITION OF CHROME LEATHER FROM COWHIDES TREATED WITH ACRYLONITRILE OR ACRYLAMIDE

	NaOH Applied with	Acrylo-nitrile	Acryl-amide	Chrome Complex	Hide Subs.	Sum	Millimoles Monomer per g. Collagen
		Percent on dry basis					
Cationic tannage							
	Na_2CO_3	—	—	21.9	78.8	100.7	—
	Na_2SO_4	—	—	21.9	79.5	101.4	—
	Na_2CO_3	5.6	—	18.1	78.1	101.8	1.4
	Na_2SO_4	4.8	—	17.4	79.0	101.2	1.1
	Na_2CO_3	—	4.1	18.9	74.6	96.7	0.8
	Na_2SO_4	—	4.1	18.7	73.6	96.4	0.8
Noncationic tannage							
	Na_2CO_3	—	—	29.8	74.2	104.0	—
	Na_2SO_4	—	—	27.7	75.0	102.7	—
	Na_2CO_3	5.8	—	20.2	74.6	100.6	1.5
	Na_2SO_4	5.3	—	20.4	75.0	100.7	1.3
	Na_2CO_3	—	3.1	25.5	73.3	101.6	0.6
	Na_2SO_4	—	3.1	33.6	66.4	103.0	0.6

high as the takeup of acrylamide. In the first experiment, however, in which steerhide was treated with the monomers for 20 hr., the fixation in millimoles/g. collagen was the same for both, e.g., 1.4 after the cationic and 1.0 after the noncationic tannage. The longer reaction time benefited the takeup of acrylamide alone. Acrylonitrile, on the other hand, unstable as it is, shows no better fixation with time or concentration.

Influence of monomer upon aldehyde binding capacity.—Table I shows that after reacting with acrylonitrile or acrylamide first and subsequent tannage with formaldehyde, steerhide shrinks at 64° and 72° C. respectively. The fixation of H_2CO by these hide pieces amounted to 22 and 35 % respectively of the quantities applied. Thus, in contrast to the T_s, formaldehyde fixation was not impaired at all by the presence of the monomer. In the case of acrylamide the affinity appeared to be even higher than that of normal cowhide, which, at the most, fixed 21% of the H_2CO applied (4). In relation to the hide substance present in this modification nearly 1.1 millimoles/g. were fixed, i.e., a quantity of H_2CO which, according to earlier findings (15), needed a much higher ratio of aldehyde to collagen.

DISCUSSION

The attachment of acrylonitrile and acrylamide to collagen causes a considerable reduction in T_s and curtails maximum chrome fixation. Although reaction conditions are fairly drastic, dry strength of the tanned leather is not affected. Therefore, we can assume that no degradation takes place under the conditions employed for the reaction of hide with the monomers, beyond the slight weakening of the fiber caused by the alkalies themselves. The present study does not provide the full answer to the question, Which active groups of the collagen molecule participate in the fixation of acrylonitrile or acrylamide? The most reactive groups, at the high pH required, are the ε-amino group of lysine and hydroxylysine residues; the guanidyl group, although considered very inert by comparison, can be partially diazotized (14*b*, 16) and at high pH values has also a remarkable affinity for formaldehyde (17). It is conceivable, however, that the guanidyl group does not participate to the same degree in the fixation of acrylonitrile or acrylamide. When alpha amino acids (18) or glycylglycine (19) are cyanoethylated, both hydrogens of the amino groups are substituted with ease. If this also is the case in collagen, a total of nearly 0.8 millimoles per gram collagen may combine in this manner, while only 0.3 millimoles at the most are left over for guanidyl residues. The tendency of forming ether links with hydroxyl groups appears to be negligible. A tricyanoethyl tyrosine was obtained in poor yield after 28 hr. of refluxing in a solution of caustic alkali (18*b*). At room temperature, in the presence of an insoluble protein, the conditions appear extremely unfavorable for this kind of substitution.

The nitrile group of a cyanoethylated material is very stable. It cannot be hydrolyzed without detriment to the long-chain molecules to which it is attached. Amide groups are more reactive. Carbamoylethylated collagen, therefore, might assume practical importance. It is able, for instance, to fix additional quantities of aldehyde. Its influence upon the fixation of vegetable or synthetic tannins has not been studied as yet.

Other advantages of acrylamide are that it is a crystalline solid, while acrylonitrile is a low boiling, highly toxic liquid. The solubility in water, of acrylamide as well as its stability at high pH values is very much greater than that of acrylonitrile. For operations on a larger scale acrylonitrile requires a completely closed system.

Acrylonitrile and acrylamide will probably not for long remain the only monomers which can be reacted with collagen under proper alkaline conditions. It also appears desirable to study the reactivity of collagen in other caustic solutions than those employed in this study. A third avenue of approach for the purpose of increasing the affinity of collagen for monomers would be the use of solvent systems which have shown promise in connection with a number of tannages.

SUMMARY

Strongly alkaline solutions in which the swelling of native hide is intentionally minimized offer satisfactory conditions for the cyanoethylation and carbamoylethylation of collagen. Under these conditions amounts as high as 1.4 millimoles per gram of collagen of either acrylonitrile or acrylamide have been introduced into the collagen molecule. The substitution with acrylamide appears to open possibilities of additional modifications; preliminary experiments point to an increased affinity for formaldehyde. Despite the fact that the maximum binding capacity for chrome and the thermal resistance are reduced, the strength properties are not affected. Finally, reasons are given why ε-amino groups are believed to be primarily responsible for the reaction with the two monomers.

REFERENCES

1. Bikales, N. M., J. J. Black, and L. Rapoport. *Text. Res. J.*, **27**, 80 (1957).
2. (*a*) Compton, J., W. H. Martin, and R. P. Barber. *Ibid.*, **26**, 47 (1956). (*b*) MacGregor, J. H. *J. Soc. Dyers and Colourists*, **67**, 66, 74 (1951).
3. Frick, J. W., W. A. Reeves, and J. D. Guthrie. *Text. Res. J.*, **27**, 92, 94 (1957).
4. Seligsberger, L., and C. Sadlier. *JALCA*, **52**, 2 (1957).
5. (*a*) Gustavson, K. H. *J. Am. Chem. Soc.*, **74**, 4608 (1952). (*b*) Erdmann, H. *Das Leder*, **7**, 198 (1956). (*c*) Küntzel, A., and H. Erdmann. *Ibid.*, 206.
6. Mann, C. W., and C. P. Merhib. *JALCA*, **50**, 584 (1955).
7. Zacharias, W. B., C. W. Mann, E. T. Steiner, and F. C. Horkowitz. *JALCA*, **48**, 460 (1953).
8. Journeay, G. E., and J. E. Blackmon. *Text. Res. J.*, **27**, 166 (1957).
9. Bowes, J. H., and R. H. Kenten. *Biochem. J.*, **43**, 365 (1948).

10. Highberger, J. H., and C. E. Retzsch. *JALCA*, **33**, 341 (1938.)
11. Kanagy, J. R. *JALCA*, **52**, 142 (1957).
12. Gustavson, K. H. *Chemistry of Tanning Processes* (New York: Academic Press, 1956) (*a*) 246, (*b*) 171.
13. ———. *Acta Chem. Scand.*, **9**, 1049 (1955).
14. ———. *Chemistry and Reactivity of Collagen* (New York: Academic Press, 1956) (*a*) 205, (*b*) 253.
15. (*a*) McLaughlin, G. E., and E. R. Theis. *Chemistry of Leather Manufacture*, A.C.S. Monograph No. 101 (New York: Reinhold Publishing Corp., 1945) 351, table 151. (*b*) Theis, E. R., and M. M. Lams. *J. Biol. Chem.*, **154**, 87 (1944).
16. (*a*) Gustavson, K. H. *JALCA*, **50**, 239 (1955). (*b*) Cassel, J., E. McKenna, and A. Glime. *Ibid.*, **48**, 286 (1953).
17. Gustavson, K. H. *JALCA*, **43**, 744 (1948).
18. McKinney, L. L., E. H. Uhing, E. A. Setzkorn, and J. C. Cowan. *J. Am. Chem. Soc.*, (*a*) **72**, 2599 (1950); (*b*) **73**, 1641 (1951).
19. Terent'ev, A. P., and P. F. Butskus. *Doklady Akad. Nauk. S.S.S.R.*, **97**, 851 (1954); abs. *Chem. Abstr.*, **49**, 10312 (1955).

Received August 23, 1957.

It is interesting to note that the real invention which made chrome leather a success, the fat liquoring process, was not patented, but was kept secret. With the present day knowledge of the chemistry of the chrome process, it is doubtful if the courts would sustain the original Schultz process as broadly as they did, but the value of the contribution of Foerderer can hardly be overestimated. The leather which Foerderer made was a chrome tanned goat skin, now universally known as glazed kid, and the Philadelphia district has always continued to lead the world in its production.
—*Lactic Acid In Leather Manufacture*. Alan A. Claflin and Harry P. Corson. Boston: The Avery Chemical Company, 1920.

It is safe to say, whoever, that there was slight scientific study given the art and little real improvement made in a period of seven hundred years, until the great spread of interest in Natural Philosophy which occurred in the latter half of the eighteenth century. The first real advancement occurred in 1778, when David MacBride, an Irishman, was given a medal by the Royal Society for his researches on the use of sulfuric acid in plumping sole leather. It is interesting to note that this use of sulfuric acid followed very quickly the commercial production of that acid, and its passing from the stage of a curiosity of the alchemist's laboratory to an article of trade. Sequin, in France in 1795, developed the MacBride process on a larger commercial scale, and made valuable contributions to the science of the art. Most of Sequin's hypotheses on the theory of tanning have been found to be erroneous, but their promulgation advanced the scientific interest in the art, and prompted further investigations.
—*Ibid.*

STUDIES OF LEATHER FUNGICIDES

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ABSTRACT

Two series of compounds structurally related to tetrachlorohydroquinone and to 4-nitrophenol have been investigated for effectiveness as leather fungicides. Among ten compounds, all having a 2,3,5,6-tetrachlorobenzene ring in common but with different substituents on carbons 1 and 4, the most effective 1,4-combination was OH, NO_2. Replacement of NO_2 in this combination with OH, Cl, and H decreased effectiveness in that order.

Among 11 aromatic nitro compounds without the tetrachloro structure, mildew-preventive activity was also associated with the 1,4 OH, NO_2 combination. Ethers of the phenols in both series of compounds were ineffective.

Bis(4-nitrophenyl) carbonate and bis(2-chloro-4-nitrophenyl) carbonate are effective mildew inhibitors apparently because of their decomposition into the corresponding free phenols under hot and humid conditions. They are of interest as leather fungicides because they are colorless and probably nontoxic, thus alleviating some of the disadvantages of 4-nitrophenol. Analytical methods for these two compounds and data on their performance in leaching tests are given.

INTRODUCTION

During the past ten years various fungitoxic substances have been evaluated as leather fungicides at the National Bureau of Standards in a program supported by the Quartermaster Corps (1,2,3). The fungicide now being used in military footwear leathers is 4-nitrophenol. Comparatively high effectiveness and low cost make this compound the preferred leather fungicide

This paper was presented at the annual meeting of the Society for Industrial Microbiology at Stanford University, on August 29, 1957. The studies were sponsored by the Quartermaster Corps of the Department of the Army as a part of research and development project 7-65-01-003B.

at the present time. However, yellow color, solubility in water which permits leaching with loss of fungicide from leathers during service, and the necessity of imposing a maximum concentration limit of 0.4% because of possible irritating effect on human skin when present in excessive amounts, are objectionable features of 4-nitrophenol. Other and better leather fungicides are, therefore, being sought.

Tetrachlorohydroquinone has been investigated as a fungicide for leather. It is colorless, nearly insoluble in water, and according to toxicity tests by the Office of the Surgeon General, not irritating to human skin in concentration considerably higher than that permitted for 4-nitrophenol. In some laboratory tests it has been found nearly as effective as 4-nitrophenol. In others it has failed. It appears to be especially ineffective with certain types of leathers (2).

This paper presents the results of experimental work on three phases of the leather-fungicide problem:

(*a*) Effectiveness of compounds structurally related to tetrachlorohydroquinone and 4-nitrophenol.

(*b*) Permanence of some fungicides in leather. This is an important factor in observations on structure-activity relationships.

(*c*) Effectiveness of bis(4-nitrophenyl) carbonate and bis(2-chloro-4-nitrophenyl) carbonate. An analytical method for the determination of these two compounds, developed in the course of this work, is reported.

MILDEW-PREVENTIVE EFFECTIVENESS OF COMPOUNDS STRUCTURALLY RELATED TO TETRACHLOROHYDROQUINONE AND 4-NITROPHENOL

Materials and methods

Two series of compounds were investigated. One series (I) consisted of ten compounds, all having a 2,3,5,6-tetrachlorobenzene ring in common but with different combinations of substituents on carbons 1 and 4; these compounds are listed in Figure 1. The other series (II) consisted of eleven aromatic nitro compounds; these compounds are listed in Figure 2. Solutions of the compounds in organic solvents were used for deposition of the desired percentages of the compounds in leather specimens by immersion.

The solvent mixture in all cases consisted of cyclohexanone, 20% mineral oil, and trichloroethylene. Complete solution of tetrachlorohydroquinone in the concentration used for treatment of leather requires about 30% cyclohexanone in the solvent mixture, while 10% cyclohexanone is sufficient for solution of 4-nitrophenol. The solvent mixture given for tetrachloroquinone, namely, 30% cyclohexanone, 20% mineral oil, and 50% trichloroethylene was employed with all compounds of series I and also with 4-chloro-2-nitrophenol. This compound was not completely soluble in the solvent mixture

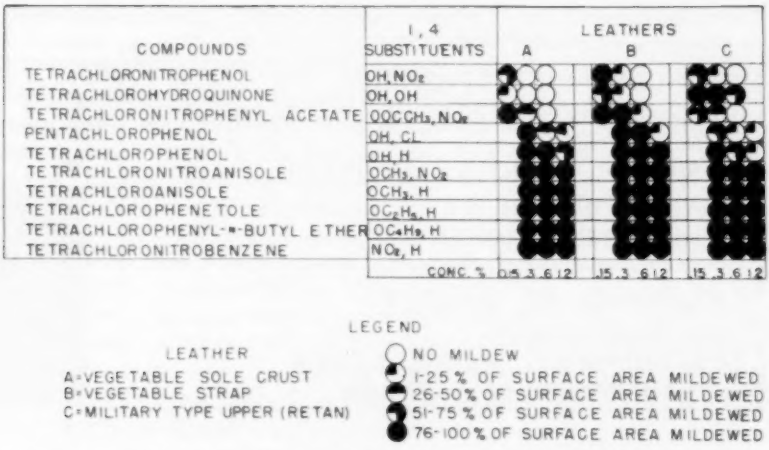


FIGURE 1.—Mildew-preventive effectiveness of 2,3,5,6-tetrachlorobenzene derivatives. Mildew growth on leathers after five weeks' exposure in a tropical room.

used with all the other compounds of series II, namely, 10% cyclohexanone, 20% mineral oil, and 70% trichloroethylene. Each compound was tested at three levels of concentration within the range 0.07–1.20%. These percentages refer to depositions in the leather based on dry-leather weight, as calculated from the average amounts of solutions absorbed by the leather, and the solution concentration. Three leather specimens were used for each concentration level of each compound.

After solvent evaporation the leather specimens were tested for mildew resistance by exposure in the tropical room at the U. S. Army Engineering Center at Fort Belvoir, Virginia, for five weeks. The amount of mildew growth was estimated visually by the portion of the surface area covered, as described in a previous publication (2).

Results and discussion

The results of the mildew-resistance tests are summarized in Figures 1 and 2.

It is quite clear from Figure 1 that the tetrachlorobenzene ring, which all the compounds listed had in common, does not confer mildew-inhibiting properties to all compounds. In the absence of certain combinations of groups on carbons 1 and 4 no inhibition occurs. The most effective combination of 1,4 substituents is OH, NO_2, when the results obtained with all three leathers are considered. When the OH group of this combination is replaced by an ester group, mildew-inhibiting potency is reduced, and when

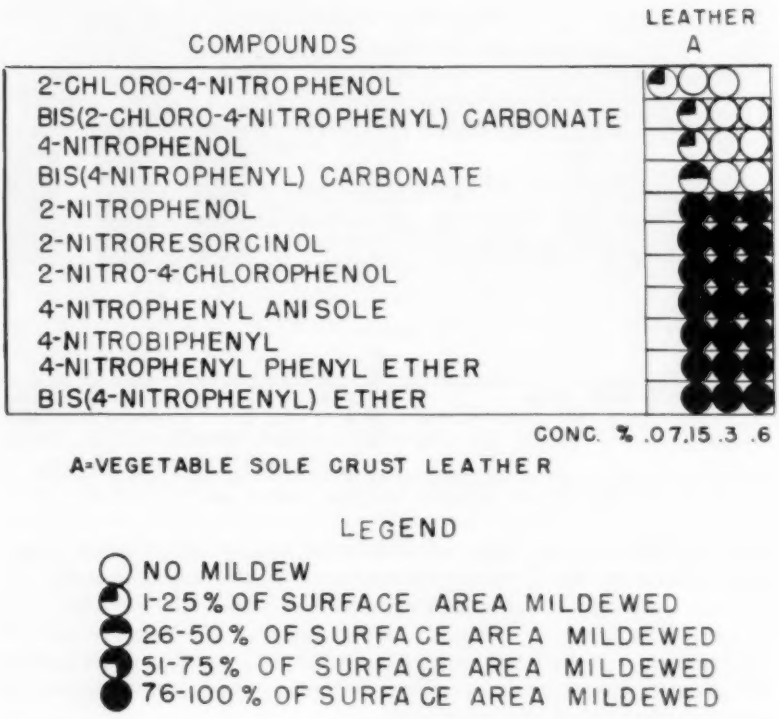


FIGURE 2.—Mildew-preventive effectiveness of aromatic nitro compounds. Mildew growth on leather after five weeks' exposure in a tropical room.

replaced by an ether group or by hydrogen, no inhibition occurs. When in this same combination (OH, NO_2) the NO_2 group is replaced by other substituents, the mildew-inhibiting potency decreases with substituents in the following order: NO_2, OH, Cl, H.

In the absence of at least one OH group no activity was observed except with one compound, the acetate ester. Probably even this compound owes its activity to regeneration of the free phenol by hydrolysis. The activity of the phenol is clearly influenced by the para substituents, a nitro group in the para position being associated with the highest mildew-inhibiting potency in this series of compounds. None of the phenolic ethers, with or without a nitro group in the para position, exhibited any mildew-inhibiting activity at concentrations up to 1.2%, which was the highest concentration used.

Among the aromatic nitro compounds listed in Figure 2, mildew-inhibiting activity was again associated with OH, NO_2 substituents in para position to each other. Addition of a chlorine, as in 2-chloro-4-nitrophenol, appears to increase the activity. Etherification of the phenol again resulted in inactivation. The bis carbonates of 4-nitrophenol and 2-chloro-4-nitrophenol were about as effective as the free phenols. As will be shown later, this is probably because these compounds decompose with liberation of the phenols. All 2-nitrophenols were ineffective, but as will be shown later, this does not necessarily mean that they are devoid of fungitoxic properties.

The relative effectiveness of compounds as leather fungicides may not be a true measure of relative fungitoxicity even if the same organisms are involved. Reaction of a fungicide with the substrate (leather and leather components) may reduce its fungitoxic potency. Under the conditions of the tropical room exposure test, which is designed to resemble service conditions, the permanence of the fungicide in the leather is also a very important factor that influences over-all effectiveness.

PERMANENCE OF FUNGICIDES IN LEATHER

It can be demonstrated that some fungicides are lost from leathers even under nonleaching conditions. The data given in Table I show the residual amounts of fungicides found in leathers one year after treatments, compared to the original amounts. These leathers had been exposed in the field for

TABLE I

PERMANENCE OF LEATHER FUNGICIDES

Fungicide	Leather*	Fungicides in Leather			Mildew Growth on Leather
		Original		1 year later	
		Calc.†	Found‡	Found‡	
4-nitrophenol	A	0.60	0.57	0.56	none
	B	0.60	0.63	0.54	none
	C	0.60	0.68	0.54	none
2-chloro-4-nitrophenol	A	0.30	——	0.11	none
	B	0.30	——	0.12	none
	C	0.30	——	0.12	none
Tetrachlorohydroquinone	A	0.60	0.60	0.45	none
	B	0.60	0.53	0.17	slight
	C	0.60	0.52	0.02	heavy
2-phenylphenol	A	1.50	1.40	0.22	moderate
	B	1.70	1.78	0.08	heavy
	C	1.10	0.73	0.04	heavy

*Leather: A=vegetable sole crust; B=vegetable strap; C=upper, chrome-retan.
†From the concentration of the fungicide in the solution used for treatment of the leathers and the weight of the solution absorbed.
‡Analytical methods: 4-nitrophenol and 2-chloro-4-nitrophenol (7), tetrachlorohydroquinone (4), 2-phenylphenol (5).

approximately 3 months but were protected from rain. They were then tested for mildew resistance by exposure for 7 weeks in the tropical room at Fort Belvoir. Some leaching action might have occurred during the tropical-room exposure by condensation of moisture from the humid atmosphere on the leathers. However, the fact that 4-nitrophenol suffered the smallest loss, although being the most water-soluble of the four fungicides listed, indicates that leaching was not responsible for the loss. The mildew susceptibilities of these samples were shown in a previous publication (2) and are also indicated in Table I. It may be seen that losses in fungicides account for lack of mildew resistance of many of the treated samples. Although more than 50% of 2-chloro-4-nitrophenol was lost, the potency of this fungicide apparently is sufficiently high that the residual amount (0.12%) was adequate for prevention of mildew growth.

One mechanism that could be expected to play a part in removal of fungicides from leather is volatilization. Especially under conditions favorable to mildew growth, i.e., hot and humid, one can visualize a process by which even a relatively nonvolatile fungicide could be removed. Changes in temperatures would expose the leather to repeated cycles of condensation and evaporation of moisture, which in effect constitutes a process of steam distillation. If the fungicide is not fixed and possesses even a slight vapor pressure, it might then be lost. In this connection it would be of interest to have data on vapor-pressure characteristics of fungicides. However, such data generally are not available.

The relative volatility of a series of compounds, including the four listed in Table I, was investigated. One-gram portions of the fungicides were

TABLE II

RELATIVE VOLATILITY OF FUNGICIDES*

Fungicide	Loss, %			Vapor Pressure† mm. Hg.
	12 hr.	120 hr.	360 hr.	
Bis(2-chloro-4-nitrophenyl) carbonate	0.03	0.04	0.04	
Tetrachlorohydroquinone	0.20	0.20	0.31	
Bis(4-nitrophenyl) carbonate	0.18	0.27	0.54	
4-nitrophenol	0.09	0.18	1.14	
4,6-dinitro-2-methylphenol	1.16	1.84	3.36	0.03 at 50°C. 0.46 at 100°C.
2-chloro-4-nitrophenol	1.28	2.07	8.42	
2-phenylphenol	3.81	9.21	38.40	1 at 100°C.
4-chloro-2-nitrophenol	32.90	51.76	97.05	
2-nitrophenol	99.09	99.89	99.93	1 at 50°C. 15 at 100°C.

*1 g. of the fungicide exposed in a shallow aluminum dish in a forced-draft oven at 40 C.
†From literature (6).

spread evenly over the bottom of cylindrical aluminum drying dishes about 6 cm. in diameter and 1.5 cm. deep. The dishes containing the fungicides were placed in a forced-draft oven maintained at 40° C. After intervals of 12, 120, and 360 hr. the dishes were removed, covered, cooled in a desiccator, and weighed. The losses in weight were calculated as percentages of the original weight.

The results are given in Table II, where the fungicides are arranged in order of increasing losses. The losses correlate with vapor-pressure data found in the literature (6) for three of the compounds.

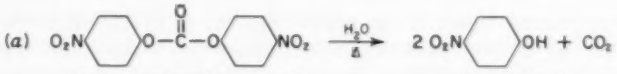
2-nitrophenol is by far the most volatile compound of those listed, 99.1% being lost in 12 hours' heating at 40° C. This explains some contradictory results we have observed with 2-nitrophenol in the past. This compound has always been devoid of any mildew-preventive effectiveness when leathers treated with it have been tested for mildew resistance by exposure in the tropical room at Fort Belvoir, (*see* Fig. 2.) However, when leathers similarly treated were tested for mildew resistance by exposure in closed humidity jars, 2-nitrophenol was about as effective as 4-nitrophenol. Undoubtedly the ineffectiveness of 2-nitrophenol under the tropical-room exposure conditions is simply due to its rapid loss by volatilization and not because it lacks fungitoxicity. In a closed container the volatile fumes are forced to remain in contact with the leather which thereby is protected from mildew growth.

Except for tetrachlorohydroquinone, the fungicides listed in Table I according to increasing losses as shown by analyses fall in the same order in Table II where they are listed according to increasing volatility losses at 40° C. This indicates that the mechanism by which 2-chloro-4-nitrophenol and 2-phenylphenol is removed from leathers probably involves volatilization. The loss of tetrachlorohydroquinone on the other hand apparently involves some other mechanism. This compound is quite nonvolatile according to the results shown in Table II. The permanence of 4-nitrophenol in leather under nonleaching conditions is probably due to a combination of relatively low volatility and fixation in leather through hydrogen bonding. Evidence for fixation of 4-nitrophenol is found in the observation that it cannot be completely extracted from some leathers with chloroform unless there is some water present (8). The relative permanence of 4-nitrophenol in leather helps to explain its unusual effectiveness as a leather fungicide compared to other equally or more fungitoxic materials.

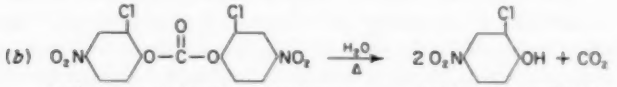
BIS(4-NITROPHENYL) CARBONATES

Bis (4-nitrophenyl) carbonate and bis (2-chloro-4-nitrophenyl) carbonate (hereafter sometimes called bis compounds in this report) are about as effective leather fungicides as the corresponding nitrophenols, i.e., about 0.30% deposition in leather prevented mildew growth in the tropical-room exposure

(Figure 2). These two compounds are not readily volatilizable (Table II), not colored, and comparatively insoluble in water at room temperature. According to preliminary findings by the Office of the Surgeon General, leathers treated to contain 1.20% bis(4-nitrophenyl)carbonate were not irritating to human skin. Since these compounds seemed to offer some definite advantages over 4-nitrophenol, they were investigated further. Their effectiveness as leather fungicides is in contrast to the general inertness of similar compounds lacking a free phenolic OH group. It seemed probable that their effectiveness is due to hydrolytic decomposition to the free nitrophenols under mildew-growing conditions. The postulated hydrolysis may be represented as follows:



bis(4-nitrophenyl)carbonate — 4-nitrophenol

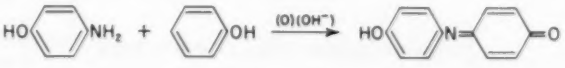


bis(2-chloro-4-nitrophenyl)carbonate — 2-chloro-4-nitrophenol

An analytical method is available for the determination of 4-nitrophenol in leather (7). As will be shown, it is equally applicable to 2-chloro-4-nitrophenol. By the use of this method the presence of the free nitrophenols could be established in leathers treated with the bis compounds and exposed to hot and humid conditions, thus providing evidence of the postulated decomposition. Further evidence on this point was obtained during development of an analytical method for the bis compounds. A slight modification of the 4-nitrophenol procedure permits its use for the bis compounds.

Analytical method

The colorimetric method used for determination of 4-nitrophenols (7) is based on the development of an indophenol blue color produced by the reduction of 4-nitrophenol to 4-aminophenol and subsequent coupling of the latter with phenol under alkaline oxidative conditions.



The fungicide is extracted from leather with chloroform. An aliquot of the extract is shaken with a 10% solution of sodium citrate to transfer the fungicide from the chloroform phase to the aqueous phase. Reduction of the 4-nitrophenol to 4-aminophenol is then made by treatment with a titanous

chloride solution. Addition of a 9.6 pH borate buffer and the phenol reagent allows the reaction to go to completion.

The two bis compounds in chloroform solution gave a light green color rather than the indophenol blue when substituted for 4-nitrophenols in this procedure. Other aromatic nitro compounds were tested to determine what specific structure is necessary to obtain the indophenol reaction product.

TABLE III

COLORS PRODUCED WITH VARIOUS NITRO COMPOUNDS IN THE TEST FOR 4-NITROPHENOL (7)

(2 ml. of chloroform solution containing 0.2 mg. of the compound was used as sample in all cases.)

	Compound	Color
1.	4-nitrophenol	Blue
2.	2-chloro-4-nitrophenol	Blue
3.	3,5-dimethyl-4-nitrophenol	Slight orange
4.	4-nitroanisole	No color
5.	4-nitrobenzoic acid	No color
6.	2,3,5,6-tetrachloro-4-nitrophenol	Slight purple
7.	2,3,5,6-tetrachloronitroanisole	No color
8.	2,3,5,6-tetrachloronitrophenyl acetate	No color
9.	4-nitrobiphenyl	No color
10.	4-nitrophenyl phenyl ether	No color
11.	Bis(4-nitrophenyl)ether	No color
12.	Bis(4-nitrophenyl)carbonate	Green
13.	Bis(2-chloro-4-nitrophenyl)carbonate	Green
14.	Bis(4-nitrophenyl)disulfide	No color
15.	Bis(2-nitrophenyl)disulfide	No color
16.	2-nitrophenol	Yellow
17.	2-nitroresorcinol	Slight yellow
18.	3,5-dinitro-2-cresol	Slight orange

The results given in Table III show that only 4-nitrophenol and 2-chloro-4-nitrophenol gave the typical indophenol color. Apparently a free hydroxyl group with a nitro group in para position to it is the specific structure that is necessary for the reaction to occur. Esters or ethers of 4-nitrophenol or nitrophenols with the nitro group in any other position than para to the hydroxyl group did not give the color. Even when a free hydroxyl and a nitro group are in para position to each other, the color is not given when certain substituents adjacent to the nitro group are present, as observed with 3,5-dimethyl-4-nitrophenol (compound No. 3 in Table III) and 2,3,5,6,-tetrachloro-nitrophenol (compound No. 6). With these two compounds steric hindrance phenomena probably prevented the color formation.

Since the bis compounds did not produce the indophenol color, they evidently did not decompose into the free nitrophenols in chloroform solution.

However, when the sodium citrate sample mixture was heated and then cooled before reduction with titanous chloride, the blue color was produced with the bis compounds also, showing that hydrolysis to free nitrophenols had occurred. It was found that boiling the mixture for ten minutes resulted in quantitative hydrolysis, as shown in Table IV. This modification was therefore introduced into the procedure to make it applicable to bis compounds in chloroform solution.

TABLE IV

EFFECT OF VARIATIONS IN HEATING OF SODIUM CITRATE–SAMPLE MIXTURE

(*5 ml. of chloroform solution, containing 0.5 mg. of the compound, was used as sample in all cases.*)

Heating	Color, Photometer Reading*	
	Bis (4-nitrophenyl) Carbonate	Bis (2-chloro-4-nitrophenyl) Carbonate
No heating	green, no reading	green, no reading
Steambath 5 min.	green-blue 22.5	green-blue 8.0
Steambath 10 min.	blue 58.0	blue 31.0
Steambath 20 min.	blue 60.0	blue 54.0
Steambath 50 min.	blue 63.0	blue 59.0
Steambath 60 min.	blue 70.0	blue 62.0
hot plate, boiled 10 min.	blue 79.0	blue 69.0
hot plate, boiled 15 min.	blue 78.0	blue 69.0

*Scale reading, Fisher electrophotometer, 650 millimicrons filter.

Absorption spectra and calibration curves.—In the procedure for determination of 4-nitrophenol in leather the colorimetric reading obtained on the aliquot of the chloroform leather extract is evaluated by reference to a calibration curve. Usually this calibration curve is constructed from colorimetric readings obtained on aliquots of an aqueous alkali standard solution containing 0.1 mg. of the fungicide per ml. This solution is prepared by tenfold dilution with distilled water of a concentrated (1 mg/ml) standard solution of the fungicide in 0.05*N* sodium hydroxide.

Both 4-nitrophenol and 2-chloro-4-nitrophenol are readily soluble in 0.05*N* sodium hydroxide at room temperature. The two bis compounds, however, are not. Heating on the steam bath was necessary to make these compounds go into solution when preparing the concentrated standard solutions. On cooling, the compounds did not reprecipitate, and the solutions had the yellow color typical of alkali solutions of the free nitrophenols.

When aliquots of the dilute standard solutions prepared as described were used as samples in the test procedure, the same blue color obtained with the 4-nitrophenols was also obtained with the bis compounds. The absorption

spectra shown in Figure 3 (a Beckman spectrophotometer was used) verify this. The curves for all four fungicides show a maximum absorption at 630 millimicrons, proving conclusively that the same reaction product was obtained with all four fungicides. Hydrolysis of the bis compounds to the free nitrophenols therefore must have occurred.

As the absorption band is wide, accurate color measurements can be made within about ± 30 millimicrons of the maximum. The curve for the "blank" (2 ml. of chloroform extract of a vegetable-tanned leather containing

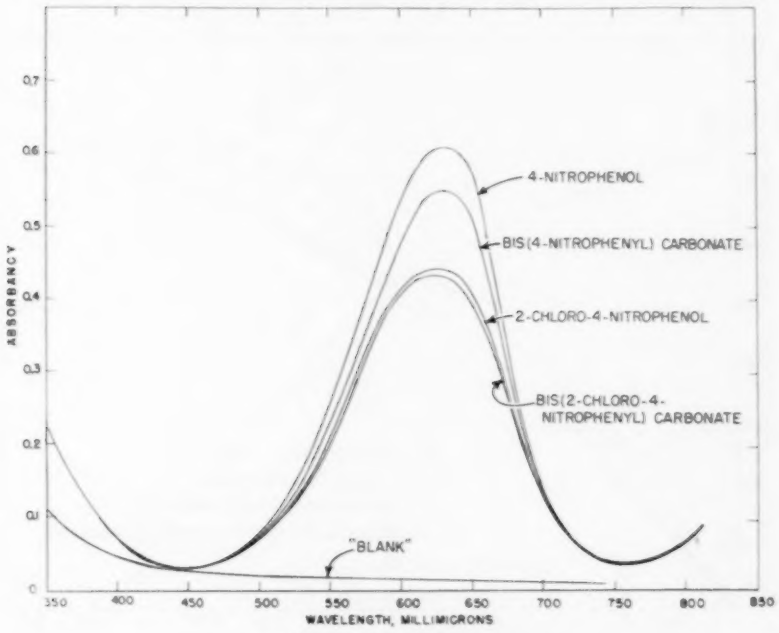


FIGURE 3.—Absorption spectra.

no fungicide) shows that other chloroform-extractable leather components do not interfere with the color measurement.

Calibration curves for the four fungicides are shown in Figure 4. These curves were also obtained with the standard aqueous alkali solutions. The colorimetric measurements (made with a Fisher electrophotometer using a 650-millimicron filter) are plotted against milligrams of the respective compounds obtained in the solutions.

In Figure 5 the sample concentrations are given in milliequivalents of NO_2 instead of milligrams. When plotted in this way it is seen that all points, with-

in experimental error and allowing for variations in purity of the compounds, fall on the same curve. (The two nitrophenols were Fisher Chemical Company's "White Label" products. The two bis compounds were of unknown purity.) Obviously, both NO_2 groups of the bis compounds participated in the reaction producing the indophenol blue color. It is clear, therefore, that each molecule of the bis compounds must have produced two molecules of the free nitrophenols, in accordance with the postulated hydrolytic decomposition.

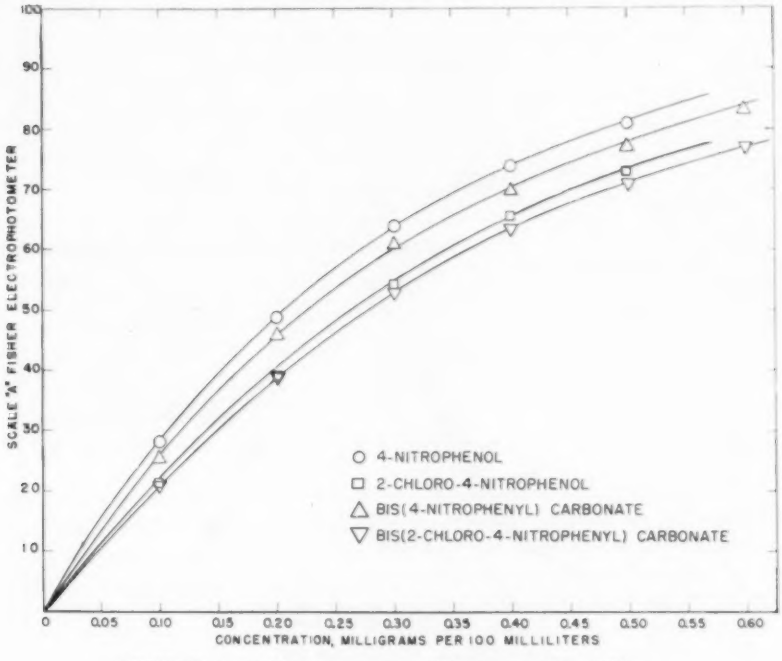


FIGURE 4.—Calibration curves, milligrams per 100 milliliters.

Recovery of known amounts of the fungicides added to leather samples.—In the 4-nitrophenol procedure the fungicide is extracted from leather with chloroform in a Soxhlet-type apparatus. The applicability of this extraction procedure to 2-chloro-4-nitrophenol and the two bis compounds was determined as follows:

2.5-gram samples of leathers were placed in extraction thimbles, and measured amounts of standard solutions of the fungicides in chloroform were added so that the leather absorbed all of the solution. The thimbles and

contents were then placed near a hot plate for evaporation of the solvent and allowed to stand for 48 hours so that any fixation of the fungicide in the leather might occur. Extraction with chloroform and determination of the fungicides were then performed as in the 4-nitrophenol procedure except that the modification of boiling the sodium citrate sample mixture for 10 minutes was employed with the bis compounds. Without this modification a green color was obtained as in the previous experiment with chloroform solutions. Evidently boiling of the chloroform extract during the extraction process did not split the bis compounds into the free phenols. The results obtained in

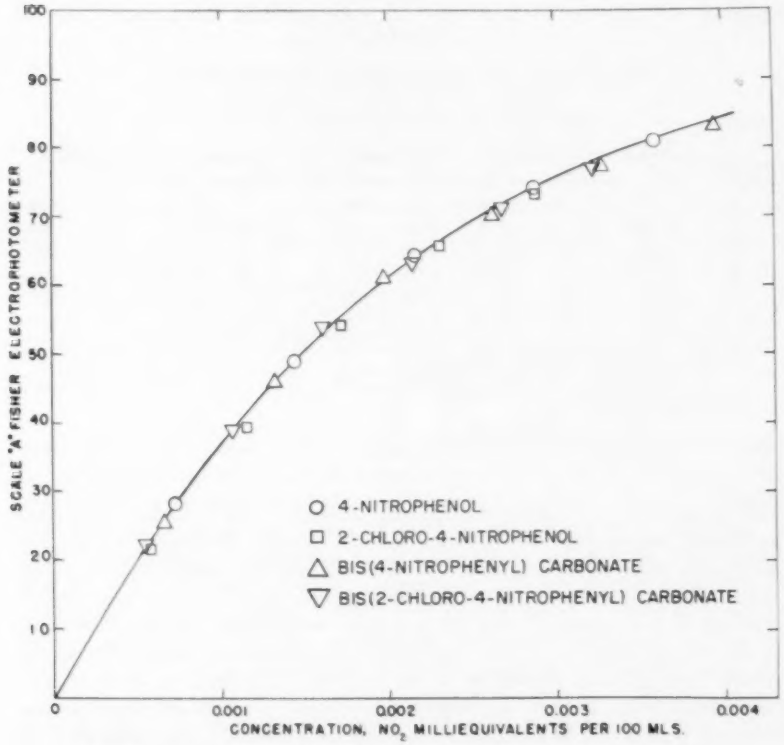


FIGURE 5.—Calibration curves, NO_2 milliequivalents per 100 milliliters.

these experiments with the three experimental fungicides and with 4-nitrophenol are given in Table V.

The results show that within the probable experimental errors quantitative recoveries were obtained with all four compounds.

Practical aspects

From the preceding observations it seems likely that the effectiveness of the bis compounds as leather fungicides is due to their hydrolysis to nitrophenols. In the carbonate forms they are probably inactive, as is the case with similar structures lacking a free hydroxyl group. Presumably they are also less toxic to human skin than the phenols, so that their concentration in the leather would not need to be carefully controlled. Their hydrolysis to phenols is facilitated by hot and humid conditions and conceivably would take place only under such conditions. These compounds, therefore, offer the

TABLE V

RECOVERY OF KNOWN AMOUNTS OF FUNGICIDES ADDED TO LEATHER SAMPLES

Leather*	Amount added,† mg.	1‡ Found mg.	1‡ Found %	2‡ Found mg.	2‡ Found %	3‡ Found mg.	3‡ Found %	4‡ Found mg.	4‡ Found %
A	2.00	2.00	100.0	2.00	100.0	2.13	106.5	2.00	100.0
A	10.00	9.75	97.5	9.75	97.5	10.25	102.5	9.38	93.8
B	5.00	5.12	102.4	4.88	97.6	5.37	107.4	5.00	100.0
B	7.00	7.25	103.6	7.25	103.6	7.50	107.1	7.25	103.6
C	4.00	4.38	109.5	4.25	106.3	4.25	106.3	4.13	103.3
C	6.00	6.38	106.3	6.25	104.2	6.38	106.3	6.25	104.2

*Leather: A=vegetable-tanned sole leather crust
B=vegetable-tanned strap leather
C=military-type upper leather (chrome retan)
†As aliquot of a chloroform standard solution.
‡Compounds: 1=4-nitrophenol
2=2-chloro-4-nitrophenol
3=bis(4-nitrophenyl)carbonate
4=bis(2-chloro-4-nitrophenyl)carbonate

unique possibility of incorporating into leathers inert, colorless, and comparatively water-insoluble substances that become fungitoxic under the conditions requiring a fungicide. Whether or not this possibility can be realized in a practical way, thus overcoming some or all of the objectionable features of 4-nitrophenol, has not yet been established. It would require, in the first place, that the bis compounds not decompose appreciably in the vehicle used for their deposition in the leather. In organic solvents such as chloroform little, if any, decomposition occurs. In tannery applications, however, it may not be practical to use organic solvents. Incorporation with leather lubricants, in the manner employed with 4-nitrophenol, probably is not feasible because the bis compounds appear to be much less soluble in oils and greases. In the second place, the practical usefulness of the bis compounds would depend on their rate of hydrolysis in the leather under mildew-growing conditions. Ideally, they should hydrolyze so slowly that the amount of phenols liberated would be about equal to that lost by leaching

under these conditions; thus, the maximum specification limit of the phenol in the leather would not be exceeded even when the bis compound was present in higher percentages.

Since the bis compounds are less soluble in water, they should be more resistant to leaching than the phenols. Some experiments that have been made indicate that this is so, although the difference is slight. The results obtained are summarized in Table VI. The values given are averages based on tests with five leathers treated with the bis compounds and the phenols and leached under identical conditions. In the water extracts from the leathers treated with the bis compounds these materials could not be detected. Colorimetric readings were the same with or without the "boiling"

TABLE VI

LOSS OF FUNGICIDES BY LEACHING

(2.5 g. of ground leather in 100 ml. of distilled water for 2 hours. Leather filtered off and washed with four 20-ml. portions of distilled water.)

Fungicide	Loss, %*
4-nitrophenol	68.4
2-chloro-4-nitrophenol	56.3
Bis(4-nitrophenyl)carbonate	53.7
Bis(2-chloro-4-nitrophenyl)carbonate	47.3

*Percent of original amount in leather. The values given are avetages based on leaching tests on five types of leather.

modification of the analytical procedure. This indicates that decomposition to free phenols preceded removal of the bis compounds, i.e., that their leaching characteristics are determined by their rates of hydrolysis. Thus, hydrolytic instability is an important factor in the behavior of the bis compounds as leather fungicides. It accounts for their potency and also for their leachability. From the point of view of potency it is an advantage; from that of leachability, a disadvantage. Possibly a 4-nitrophenyl complex that would behave in the same manner as the bis (4-nitrophenyl)carbonates but be slightly more stable would be even more advantageous as a leather fungicide.

The bis compounds are not now commercially available. Whether or not they can be made available at a price competitive with 4-nitrophenol has, of course, an important bearing on their practical use as leather fungicides.

ACKNOWLEDGMENT

The authors are indebted to the Columbia–Southern Chemical Corporation for many of the compounds having the 2,3,5,6-tetrachloro configuration, and to the Allied Chemical and Dye Corporation for the bis compounds.

The permission of the Office of the Chief of Engineers, U. S. Army, to use the tropical room at the Engineering Center, Fort Belvoir, Virginia, is greatly appreciated.

REFERENCES

1. Dahl, S. *JALCA*, **51**, 103 (1956).
2. ——— and A. M. Kaplan. *JALCA*, **51**, 118 (1956).
3. ——— — ———. *JALCA*, **52**, 536 (1957).
4 ———. *Anal. Chem.*, **25**, 1724 (1953).
5. Gottlieb, S., and P. B. March. *Ind. Eng. Chem., Anal. Ed.*, **18**, 16 (1946).
6. Jordan, T. Earl. *Vapor Pressure of Organic Compounds* (New York: Interscience Publishers, 1954).
7. Lollar, R. M. *JALCA*, **45**, 728 (1950).
8. ———. *JALCA*, **49**, 605 (1954).

Received October 19, 1957.

Dr. Lewis, an English chemist, was perhaps the first to attempt the quantitative assay of tanning materials, and Sir Humphry Davy, the foremost chemist of the early decades of the last century, gave much attention to the chemistry involved in the tanning processes. Davy analyzed and classified many of the natural tanning materials, corrected and exploded many misconceptions of the art of tanning and generally elevated its character.

—*Lacitic Acid In Leather Manufacture*. Alan A. Claflin and Harry P. Corson. Boston: The Avery Chemical Company, 1920.

The tanning industry is particularly indebted to Mr. Jackson S. Schultz, an American tanner, who, about 1877, published a series of papers on tanning in the *American Shoe and Leather Reporter* which were afterwards published in book form. By sheer force of reason and intelligent observation, Mr. Schultz anticipated much that modern chemistry has since corroborated. Perhaps the greatest contribution was the development of the manufacture and use of tanning extracts, which has enabled American heavy leather tanners to retain the preeminence they originally obtained by the abundance of hemlock bark and of cheap, range cattle.

—*Ibid.*

In 1889, an American patent was granted to Augustus Schultz, a German dye chemist who was employed by the New York agents of a German firm, for a method of tanning leather by the use of compounds of chromium. This invention marked a new epoch in the tanning history of the world. Today from eighty to ninety per cent of all the upper or light leather which is manufactured is chrome tanned, and were it not for the fact that the superior quality imparted by the chrome tannage made available for shoe purposes skins which otherwise could hardly be used for such purposes, it would seem that a large part of the civilized world would be going barefoot.

—*Ibid.*

LIFE LINES

Brief Biographies of Our Contributors

HUBERTINA D. CLAYTON was graduated from the University of Philadelphia with a master of science degree in biochemistry after having completed her undergraduate work in biology and chemistry at Seton Hill College, Greensburg, Pa. She has been active in research on tanning and leather development since 1952 in the Leather Technology Laboratory Branch of the Quartermaster Research and Engineering Command.

F. L. COLLINS ("LES") graduated from the University of Florida in 1928. In the same year he joined International Shoe Company where he has worked ever since. For the last 13 years he has served on the staff of International's Cherokee Laboratory in St. Louis, and now he is Assistant Director. He joined ALCA in 1930 and served as a Member of Council from 1952 to 1954.

SVERRE DAHL.—See the April, 1957, *Journal.*

MARTIN L. FEIN.—See the January, 1957, *Journal.*

DR. EDWARD M. FILACHIONE.—See the November, 1956, *Journal.*

EDWARD H. HARRIS, JR.—See the November, 1956, *Journal.*

DR. ARTHUR M. KAPLAN.—See the October, 1957, *Journal.*

ALFRED H. KORN.—See the September, 1956, *Journal.*

DR. JOSEPH NAGHSKI is Head of the Hides, Tanning Materials and Leather Section of the Eastern Utilization Research and Development Division of the United States Department of Agriculture. He received his B.S. degree from Cornell University, the M.S. degree from the University of New Hampshire, and his Ph.D. degree from Pennsylvania State University. He joined the staff of the United States Department of Agriculture's Eastern Regional Research Laboratory in 1941 where he has carried out research in various fields which include chemistry and microbiology of tobacco fermentation, chromatography of tobacco alkaloids, chemistry of flavonoids, chemistry and microbiology of maple sugar products, and microbiological processes for recovery of natural rubber. He is coauthor of a recent book entitled *Rutin and Related Flavonoids.* In 1955 Dr. Naghski was appointed Head of the Hides, Tanning Materials and Leather Section of the Eastern Regional Research Laboratory, which is now part of the Eastern Utilization Research and Development Division. In the same year he became an active member of ALCA.

G. M. Oliensis is a graduate of Washington University, St. Louis. After brief employment with L. D. Le Gear Veterinary Medicine Company and two years in the army, he went with International Shoe Company's Cherokee Laboratory (St. Louis) in 1946. He became an ALCA member in 1950.

Dr. Ludwig Seligsberger is Chief of the Synthetic Tanning Evaluation Section of the Leather Technology Laboratory Branch of the Quartermaster Research and Engineering Center in Natick, Mass. Further biographical data were given in the January, 1957, number of *JALCA*.

Dr. P. A. Wells is the Director of the Eastern Utilization Research and Development Division of the United States Department of Agriculture. He received his B.S. degree from the University of Minnesota, the M.A. degree from George Washington University, and his Ph.D. degree from Georgetown University. His entire career has been devoted to the United States Department of Agriculture. He began his career as a research chemist in the former Bureau of Chemistry and Soils in 1928. He was appointed Director of the newly organized Eastern Regional Research Laboratory of the Department of Agriculture in 1939. This laboratory later became part of the Eastern Utilization Research and Development Division with Dr. Wells as Director. In addition to his research achievements in fermentation chemistry Dr. Wells has been widely recognized for his leadership as a research administrator. In 1953 he was awarded an honorary D.Sc. degree by the Philadelphia College of Pharmacy and Science and in 1955 by Monmouth College. In 1956 he also received the Department of Agriculture's Distinguished Service Award.

The invention of Mr. Frank Wayland, a leather Splitter of Salem, Massachusetts, contributed greatly to the successful production of chrome side leather. It made possible the green splitting of hides, or splitting the hide out of the lime, bate or pickle instead of when partially tanned, and thus made possible the tanning of the grain by the chrome process, and of the split by a vegetable tannage. A still further improvement in the chrome tannage has been the use of the acid fat liquor. Whereas in Foerderer's original fat liquor, soap was used as the emulsifying agent, in the acid fat liquor a sulfonated oil is used, which insures more even and brilliant coloring.

—*Lactic Acid In Leather Manufacture*. Alan A. Claflin and Harry P. Corson. Boston: The Avery Chemical Company, 1920.

To Prevent Boots and Shoes from Squeaking, rasp with a coarse rasp the outsole and insole, and every other piece of leather that is moved by the action of the foot. Then apply freely good wheat or rye paste. If this is well attended to from heel to toe, the boot or shoe will not squeak.

—*The Techno-Chemical Receipt Book*, ed. by W. T. Brannt and W. H. Wahl. Philadelphia: Henry Carey Baird & Co., 1892.

ALCA NEWS

Proceedings, Reports, Notices, and News

of the

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OBITUARY

William R. McCreary, an active member of ALCA, died very suddenly on October 31, 1957, at the age of 56. Mr. McCreary was employed by J. S. Young Company and previously had been associated with Taylor White Extracting Company.

ABSTRACTS OF 1958 CONVENTION PAPERS DUE FEBRUARY 28

The Chairman of the 1958 Annual Meeting Committee earnestly requests all members who intend to present papers at the 1958 Annual Meeting to submit short abstracts of such papers not later than February 28, 1958. Compliance with this request will greatly aid the committee in arranging the program. Abstracts should be mailed to the chairman of the Convention Committee, Clinton E. Retzsch, c/o Nopco Chemical Co., Harrison, N.J.

CANDIDATES FOR THE 1958 ELECTION

CANDIDATES FOR PRESIDENT-ELECT

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The above slate of candidates has been prepared by the Nominating Committee.

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Carl Telander
R. M. Lollar, *Chairman*

Members note:

Article V-2, Nominations (c)

Additional candidates may be nominated by petitions, signed by 15 or more active members. Such petitions shall reach the Secretary not later than April 1, and shall contain a statement of the willingness of the nominee to serve if elected. No member shall sign more than one petition for each office to be filled.

DIRECTORY CHANGES

NEW MEMBERS

George S. Hebb, Jr., 3 Stowell Road, Winchester, Massachusetts.
Business address: Hebb Leather Company, Inc., 112 Beach Street, Boston, Massachusetts.

J. E. Morrow, Sun Oil Company, 1608 Walnut Street, 11th Floor, Philadelphia 3, Pennsylvania.

Frank R. Simioni, Box 306, Huntsville, Ontario, Canada.
Business Address: Anglo Canadian Leather Company, Ltd., Huntsville, Ontario, Canada.

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Hugo Alps, 119 Gravel Hill Road, Huntingdon Valley, Pennsylvania.

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Richard H. Cummings, 37 Rip Road, Hanover, New Hampshire.

Herschel Eisenman, 299 South Harrison Street, East Orange, New Jersey. Business address: Globe Fur Dyeing Corporation, 521 W. 26th Street, New York 1, New York.

G. H. W. Humphreys, Inchmery, Sabrina Terrace, Thorneloe, Worcester, England.

J. Stanley Kirk, 1130 Lancaster Avenue, Reading, Pennsylvania.

Joseph A. Lancaster, Maro Leather Company, 831 Broadway, Newark, New Jersey.

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RESIGNATIONS

William K. Conn, 114 Fairview Road, Springfield, Pennsylvania.

Clarence H. Fiedler, Saxe Cutch Corporation, 500 Fifth Avenue, New York 36, New York.

Thomas G. Greaves, American Dyewood Company, Belleville, New Jersey.

A. B. Hoel, Sun Oil Company, 1608 Walnut Street, Philadelphia, Pennsylvania.

Paul C. Stahnke, 2205 Wauwatosa Avenue, Wauwatosa 13, Wisconsin.

Fred Thayer, Argo Corn Products, Argo, Illinois.

DEATHS

William R. McCreary, 33 Overington Avenue, Clementon, New Jersey.

ABSTRACTS

Microorganisms and Their Relationship to Tanning Operations. E. F. Weiss. *Leather Mfr.*, **74,** No. 4, 21 (1957).—The author, after stating that microorganisms are very small living things, gives a brief description of their size and weight, rate of growth, range of conditions under which they may still survive, and their destructive and constructive use by nature. The microorganisms, bacteria and mold, are clearly defined as well as the method by which they obtain their food and the chemical elements necessary for their growth. The part that relative humidity, pH, and temperature have on growth is also stated. Enumerated are the molds found on pickled sheepskin and the bacteria on red-stained salted hides. The places where mold has been observed in the tannery are mentioned. It is suggested that preservatives are an essential factor in the elimination of microorganism growth during the manufacturing of quality leather. J.J.

Conversion of Hydroxyproline to Pyrolle-2-Carboxylic Acid. A. N. Radhakrishnan and Alton Meister. *J. Biol. Chem.*, **226,** 559–71 (1957).—While this paper reports on metabolism of hydroxyproline, some information on the nonmetabolic oxidation with hydrogen peroxide is reported which may help establish optimal conditions for the quantitative determination of hydroxyproline by the Neuman and Logan colorimetric procedure. J.M.C.

Observations on the Presence of Plasma Proteins in Skin and Tendon. J. H. Humphrey, A. Neuberger, and D. J. Perkins. *Biochem. J.*, **66,** 390–99 (1957).—The presence of plasma proteins in extracts of skin of rat and rabbit and in extracts of tendon of rat, rabbit, and ox is demonstrated by electrophoretic and immunological methods. With injection of a labeled albumin, the crude albumin of rabbit skin is shown to resemble the circulating serum albumin. Both tendon and skin contain significant quantities (0.7% in rabbit skin) of serum proteins in addition to those present within the blood vessels. The data suggest that about 60% of the skin albumin is replaced daily by circulating serum albumin. J.M.C.

Collagen and the More Soluble Constituents of Skin. J. H. Bowes, R. G. Elliott, and J. A. Moss. *J. Soc Leather Trades' Chemists*, **41,** 249–66 (1957).—The chief constituent of skin is collagen, but experiments on extractions with dilute acid and alkaline solutions indicate the presence of a number of different protein fractions differing in solubility. The methods used for the determination of the amino acid composition and terminal amino groups of such protein fractions are briefly described. Attention is drawn to the peculiarities of the amino acid composition of collagen. No terminal amino groups are detectable in the original collagen, but after relatively mild treatments a number become available for reaction. A collagenous protein extracted from calfskin with citrate buffer is described and compared with oxhide collagen. Certain small differences in amino acid composition suggest that oxhide collagen is associated with a protein relatively rich in tyrosine, histidine, leucine, and amide nitrogen, and containing little or no hydroxyproline. Further experiments on the extraction of calfskin with citrate buffer, dilute acetic acid, and alkali indicate the presence of one or possibly two noncollagenous protein constituents closely associated with the collagen. J.M.C.

Investigations on Bating. III. The Mechanism of Bating. G. H. Green. *J. Soc. Leather Trades' Chemists*, **41**, 222–49 (1957).—The process of bating goatskin, calfskin, and oxhide was examined by microscopical and visual observation of bated versus unbated skin pieces. Progressive penetration of enzyme and rapid action, rather than rapid penetration and slow action, are said to occur. The physical and microscopical differences observed in chrome leathers produced from different bating times are diminished by drying the leather under tension. Bating, fatliquoring, and acetone dehydration in place of air-drying all yield a softer, more flexible leather. Bating and acetone dehydration result in a separation of fibers by air, whereas fatliquoring separates them by a film of oil. The effect of bating is to assist the removal of some material which, if left in the skin during tanning, predisposes the collagen fibers to stick together when the leather is dried. Substantially better bating is observed when skins are preheated in water at 40°–45°C. before bating at 27°C. The optimum pH of bating for a number of proteolitic enzymes agrees with the optimum pH for gelatinase activity. Degradation of progelatin material is necessary if it can be removed mechanically (i.e., by scudding). The following theory of bating is proposed: Collagen $\xrightarrow{\text{lime}}$ progelatin $\xrightarrow{\text{heat}}$ gelatin $\xrightarrow{\text{trypsin}}$ low-molecular-weight peptides. J.M.C.

A Study of the Mechanism of Fatty Spue Formation. II. R. G. Mitton and K. G. A. Pankhurst. *J. Soc Leather Trades' Chemists*, **41**, 161–83 (1957).—Previous work (abstr. *JALCA*, **52**, 530 [1957]) showed that migration of solid fat plays an important role in the formation of fatty spue on the grain of chrome leather. In the present experiment assessment of spue formation on chrome glove leathers tested with varying concentrations of different mordants, dyes, and fats suggests strongly that fat migration to the grain may be the result of concentration gradients in the leather. An explanation is lacking for the effectiveness of certain concentration gradients and not others. Certain dyes and mordants enhance spue formation much more than others. Factors which influence fat crystal formation play an important part in regulating the amount of spue formation. To a moderate extent the amount of spue may be modified by "seeding" the grain surface with fat crystals, by mechanical treatment of the leather such as "staking", and by thermal treatment. Oleic acid added to other fat did not repress crystallization on the leather surface. J.M.C.

The Control of Hard Spot and Red Heat on Wet-Salted Calfskins. F. W. Woodroffe, F. G. Caughley, and M. E. Pattinson. *J. Soc. Leather Trades' Chemists*, **41**, 206–16 (1957).—The present position regarding the formation of hard spot in calfskins is reviewed, and the possibility of enzymes being responsible for the release of phosphate and prevention of this by use of boric acid is discussed. Trials were made using various bactericides and boric acid as preliminary treatments prior to salt stacking. No bactericide was effective, but boric acid gave complete protection. Treatment of skins with a 2% solution of boric acid 1½ hr. before salt stacking proved most efficient. J.M.C.

The Cross-linking of Collagen with Aliphatic Epoxides. R. L. Sykes. *J. Soc. Leather Trades' Chemists*, **41**, 199–206 (1957).—A report is given of the reaction between several aliphatic, multifunctional epoxides and collagen. Butadiene dioxide, butanediol-diglycidylether, butanetriol-triglycidylether, and

glycerine-triglycidylether were evaluated. Application of the theory of rubber-like elasticity to the stress/strain characteristics of hydrothermally contracted collagen tendons before and after tannage indicated that the epoxides were cross-linking agents. The rise in shrinkage temperature was directly related to the logarithm of the number of introduced crosslinks. The epoxides produce a white leather requiring a minimum of fatliquoring but slightly inferior in strength to vegetable-tanned leather; exposure to laboratory atmosphere for six months led to no appreciable discoloration or yellowing of the leather.

J.M.C.

Modern Finishes for Leather. W. O. Nutt. *J. Soc. Leather Trades' Chemists*, **41,** 189–99 (1957).—Resin binders of the acrylic and diene types commonly used for finishing are compared in the light of finish requirements, and the effects of their components are discussed. The importance of the pigment/volume concentration requirements of different leathers is illustrated. Several tests applicable to resin binders and suitable for use in the tannery laboratory are described. J.M.C.

The Effect of Chlorination and Subsequent Dechlorination on the Tanning Properties of Ligninsulfonates. Alan G. Newcombe and H. Borden Marshall. *Can. J. Technol.*, **33,** No. 3, 152–60 (1955).—To improve the tanning properties of lignin additional phenolic groups were introduced by chlorination at low pH in the absence of light and with a halogen carrier, followed by dechlorination on heating with alkali. A waste sulfite liquor and a high-molecular-weight ligninsulfonate were treated in this manner. Ion exchange resins were used to purify the chlorinated and dechlorinated products. A series of reactions is postulated to occur during chlorination of the ligninsulfonate. The tanning properties of the ligninsulfonates, as judged by weight yield, shrinkage temperature, and grain softness and smoothness were enhanced by the chlorination and subsequent dechlorination. J.M.C.

The Light Fastness of Dyed Fibres—A Statistical Study. C. H. Giles (with an appendix by John C. Eaton). *J. Soc. Dyers and Colourists*, **73,** 127–60 (1957).—About 16,000 published commercial lightfastness assessments have been examined statistically and the results tabulated. 63 references accompany the article. R.M.L.

The Importance of Temperature and Relative Humidity in Light Fastness Testing. K. McLaren. *J. Soc. Dyers and Colourists*, **72,** 527–37 (1956).—The most important cause of anomalous results in lightfastness testing is the effective humidity during exposure. The range of effective humidities in routine testing in different fading lamps employed in Great Britain has varied from about 2% in some unscreened lamps to about 70% in the Calico Printers Assoc. lamp. These differences can cause variations in the result obtained of as much as four grades in relative fading rates. The preferred effective humidity for testing for comparison to daylight testing in Great Britain is 20%. The article points out that different conclusions may be reached if the Atlas Fade-Ometer is used without heat filters, since appreciable surface heating will then occur. Thus, at a black panel temperature of 135°F., 35 to 65% relative humidity results in an effective humidity of only 9 to 16%. Since the effective humidity is so low, the effect of temperature is more significant. R.M.L.

Precise Measurement of Fading on a Time-Intensity Basis. J. S. Mudd. *J. Soc. Dyers and Colourists*, **73,** 47–52 (1957).—A simple type of fading lamp is described using a 150-watt xenon lamp. Since the light falling on a pattern can be maintained at constant intensity for a considerable time and the intensity can be accurately measured, the fastness to light of a pattern can be precisely expressed in terms of the amount of light (kilo-foot-candle hours) required to fade the pattern to a predetermined tolerance limit of color change. R.M.L.

A Critical Appraisal of the International Daylight Fastness Test. K. McLaren. *J. Soc. Dyers and Colourists*, **73,** 121–27 (1957).—The international daylight-fastness test has been critically examined to determine its reproducibility and its reliability. Only one variable in exposure, the effective humidity, has been found to cause variations in assessment, and this is governed primarily by the proportion of sunlight falling on the pattern during exposure. It is suggested that the xenon arc, having an emmission spectrum practically identical with that of sunlight, combined with humidity control might permit development of a test method which would correlate with daylight tests made in different localities with characteristic ambient humidities. R.M.L.

Some Observations of the Absorption of Alkali by Wool Keratin from Aqueous Solutions of Sodium Carbonate and Bicarbonate. R. P. Harker. *J. Soc. Dyers and Colourists*, **73,** 17–23 (1957).—Although the pH of an aqueous extract of wool can be regarded as a measure of the combined base, it does not provide any definite information on the previous history of the wool. Thus, depending on the liquor ratio, temperature, and time of immersion, a strong bicarbonate and a weak carbonate solution could give rise to the same pH of the aqueous extract. Quantitative interpretation of the data secured in terms of the Donnan theory is attempted, but further information is needed before this interpretation can be considered satisfactory. R.M.L.

Investigation of Synthetic Tannins by Paper Chromatography. G. Vágó and I. Malovecz. *Das Leder*, **8,** 81–85 (1957).—A study was made of the window chromatographic method of Jamet (*Bull. Assoc. Franc. Chimistes Inds. Cuir*, **14,** 19 [1952]) and the ring method of Rutter (*Nature*, **166,** 273 [1950]). By the latter, which was the better of the two, a drop of the solution under investigation was put at the center of a 116-mm., S&S no. 602, filter paper disk supported in a petri dish over the eluting solution; this solution was a mixture of butanol 4 parts, glacial acetic acid 1 part, and water 5 parts. A tongue 4 mm. wide was cut to the center of the paper disk and bent down into the eluting solution. Suitable developers were the stabilized diazo compounds (Echtsalz) or the so-called Ursol dyes (paraphenylenediamine and derivatives of it). With the former, procedure was as follows: (1) spray with 0.5% ferric chloride solution, (2) dry and treat with ammonia vapor, (3) spray with a 1% solution of Echtsalz, (4) dry and treat with ammonia vapor. The colors obtained with the two developers are listed for some of the phenolic components found in syntans. The order of components in the chromatogram followed their affinity for water. Hydrophilic materials had low Rf values; hydrophobic materials, high values. The phenols on which the syntans were based and the unsulfonated novolaks had Rf values of 0.90–1.00. The Rf value is inversely proportional to a, the distribution coefficient between water and organic solvent.

Rf values decrease with molecular weight, but the influence of sulfonation is much greater than that of condensation. A paper chromatogram of Tanigan Extra KN (an HCHO condensation product of a mixture of beta-naphthol-sulfonic acid and phenol-cresol) showed 4 or 5 rings with Rf values ranging from 0.14 to 0.80. After paper electrophoresis of this syntan, stripes of the same colors were found but in the reverse order in the direction of the anode; components with lowest Rf values had the greatest number of sulfo groups and therefore moved faster to the anode. Because the phenol or its novolak moves with the solvent front, they can be detected easily in the finished syntan. For example, pyrocatechol can be detected in Basyntan Extra K and NR. The presence of unchanged pyrocatechol, after heating it with sulfite waste liquor, indicates it was not sulfonated. The same was true for the pyrocatechol-formaldehyde condensation product and naphthalene sulfo acid derivatives, but with naphthol sulfo acid no unsulfonated pyrocatechol or its unsulfonated condensation product was present. Chromatograms of sulfonated phenols contain several rings, thus showing the mixed character of the product. For example, beta-naphthol sulfonated at 100° shows rings with Rf values of 0.12, 0.23, 0.41, 0.54, and 0.65. The lower Rf values are from disulfonic acids. With a greater amount of sulfuric acid the intensity of the inner rings increases and more rings form. There is also a temperature effect. If sulfonated at 30°, o-cresol shows rings with Rf values of 0.48 and 0.71, but if sulfonated at 130°, there are rings with Rf values of 0.27, 0.51, and 0.71. Naphthalene, after sulfonation at 130°, shows rings with Rf values of 0.23 (intense), 0.47 (weak), and 0.79 (intense). These rings are found to some extent in chromatograms of all naphthalene-based syntans and are not changed by the HCHO condensation. The paper chromatographic method can be used to identify individual syntans. Products from different manufacturers may be found to be identical. I.D.C.

Spiral Drums as a Mechanizing Agent in the Leather Industry. F. Stather. *Das Leder*, **8**, 145–47 (1957).—One of the most interesting developments in the attempts of the Soviet Union to mechanize the tanning process is the entirely new spiral apparatus for treating hides in liquors. It was developed by P. W. Jawschic, and drums have been in use in several large plants for over 2 years. Units can be arranged to (*a*) wash, soak, and lime hides, (*b*) delime, pickle, tan, neutralize, fatliquor, and dye hides for chrome leather, or (*c*) tan with vegetable extracts or syntans. The larchwood drums are from 2.7 to 3.0 m. in diameter and from 16 to 20 m. long. Both ends are half-open. The drum is bound with malleable iron bands which are supported on pairs of iron rollers. The drum is driven at the middle by a 10–15 kw. motor and gear. An automatic shift permits a rocking motion through an angle of 170°–220° or a complete turn through 360°. The drum is divided throughout its length into sectors by built-in wooden or metal spirals. A drum 16 m. long for soaking and liming has 7 sectors; the first is 1.8 m. wide and the last, 2.4 m. wide. A drum 30 m. long for vegetable tanning is divided into 30 sectors which increase in width from 0.9 to 1.2 m. from tail to head. Liquor is added to the various sectors from a wooden pipe mounted in the axis of the drum. By means of a special device it is possible to move liquid from any sector to another sector or to waste without stopping the rocking. For beamhouse work 1250–1500 kg. of raw hide are rinsed for 0.5 to 1 hour and soaked 5 hours in the first two sectors with a hide-water ratio of 1:2.3. The hides are then limed for 30 hours in sectors 3 to 7, starting the liming in sector 3 with used liquor from sector 6 and some fresh

liquor. Sulfide is added to sectors 4 and 5. Continuous tanning is done by adding 500–600 kg. of white or prechromed hide to sector 1, rocking the drum through an angle of 220°, and slowly rotating the drum through one complete revolution every 2.5 hours to move the hides one sector to the right. In the first 20 sectors the tan liquor flows countercurrent to the hides (to the left) through screened holes in the spiral partition. The liquor in sector 1 is discarded. Fresh liquor is added to sectors 21 and 22. It flows with the hides in sectors 22 to 26, decreases in strength, and is pumped from 26 to 18. The leather is washed with water in sectors 27–29; the wash water is transferred to sector 9 or 10 which contain liquor of the same strength. To fill the drum requires 15,000–18,000 kg. of hide and 30,000 l. of tan liquor. For tanning, 24% of pure tannin (Soviet analysis) on the white weight is used; the liquors are carefully filtered and settled. In each sector, volume, temperature, and pH are registered automatically. Tanning temperature rises from 35°C. at the start to 42°C. at the end. The pH value increases gradually from 4.1 in sector 1 to 5.8 in sector 18, then falls to 4.2. The tannin content of the tan liquor increases from 5 g. tannin per l. in sector 1 to 100–110 g. in sector 21, then falls to about 85 g. per l. in sector 28. The total tanning time is 75–85 hours. This process has these advantages; it can be coupled to an assembly line, loading and emptying the drum are done without interrupting the operation, and there is central control of the liquors. Disadvantages are: the equipment is quite expensive; uniform liming and tanning would not be possible with nonuniform raw stock; necessary repairs stop the whole process and may endanger the stock; and only a rapid tanning process can be used, so that only leather of the quality of rapid-tanned materia' can be produced. I.D.C.

Biosynthesis of Collagen. The Influence of Ascorbic Acid on the Proline, Hydroxyproline, Glycine, and Collagen Content of Regenerating Guinea Pigskin. Bernard S. Gould and J. Frederick Woessner. *J. Biol. Chem.*, **226,** 289–300 (1957).—The possibility is posed that in ascorbic acid deficiency there may be an accumulation of a more primitive precursor than procollagen or tropocollagen, rich in proline and glycine but free of hydroxyproline. Hydroxylation of the proline presumably occurs on administration of ascorbic acid. Autoclaved extracts of granulated tissue from normal, scorbutic, and ascorbic acid–treated guinea pigs were analyzed for proline, hydroxyproline, and glycine. Seven-day depletion of ascorbic acid results in almost complete cessation of hydroxyproline formation in wounds. Depleted animals restored to ascorbic acid at the time of wounding produce the bulk of hydroxyproline between the 6th and 8th days after wounding. The rapid appearance of hydroxyproline in wounds of scorbutic animals upon administration of ascorbic acid 10 to 12 days after wounding is accompanied by a concomitant decrease in the noncollagenous proline and glycine of the granulation tissue. J.M.C.

Colorimetric Determination of Tyrosine. G. Ceriotti and L. Spandrio. *Biochem J.*, **66,** 607 (1957).—The reaction of tyrosine with α-nitroso-β-naphthol dissolved in 0.1 *N* NaOH produces a linear color response with solutions containing between 1 and 16 μg. tyrosine/ml. A standard deviation calculated four times on groups of ten samples gave a value of ± 1.5%. The method is applicable to determination of tyrosine in protein hydrolysates. J.M.C.

An Improved Method for the Microdetermination of Arginine by Use of 8-Hydroxyquinoline. G. Ceriotti and L. Spandrio. *Biochem J.*, **66**, 603–7 (1957).—The color formed by the reaction of arginine with 8-hydroxyquinoline is stabilized by extraction into butanol and the use of urea avoided. The reaction allows quantitative determination of arginine between 0.5 and 6 μg/ml; the color is stable for at least 12 hr. Results are reproducible (standard deviation $\pm$ 1.3%). J.M.C.

Effect of Certain Acid Dye Structures on the Rate of Wool Dyeing. J. H. Skinkle and E. W. Makuch. *American Dyestuff Reporter*, **46**, P578–82 1957.—The fundamental dye structure has only a small effect on the rate of dyeing, but it appreciably affects the final equilibrium dye exhaustion. The position of the sulfonic group or the shape of the dye molecule appreciably affects the rate of dyeing, but has no effect on the final equilibrium exhaustion. The greatest equilibrium exhaustion, but the lowest rate of dyeing, is obtained when the dye molecule is large; the converse is also true. In general, the data for all dyes agree fairly well with the theoretical relationship expressing the first half of the dyeing but deviate from the theoretical relationship expressing the last half of the dyeing in a manner consistent with the number of carbon rings on the dye molecule. R.M.L.

BOOK REVIEW

Hides, Skins and Leather under the Microscope. Published and distributed by the British Leather Manufacturers' Research Association, Milton Park, Egham, Surrey, England. 368 pp., 996 illus. £8 10s.—This is a most interesting and valuable contribution to our knowledge of the microscopy of skins, hide, and leathers. There is no other book to compare with it; the photomicrographs are superbly done, and each is adequately described. An introductory chapter records techniques and diagrammatic illustrations which make the histology of the photomicrographs more readily understood by persons with a minimum of training in this science. The book, as its title indicates, covers skin, hide, and leathers. It also includes the process specimens from raw stock through to finished leather, instructions for making microassessment of leather, and illustrations of many conditions found in leathers. This book should be in every tannery library. F. O'F.

CORRECTION

In the June, 1957, issue of the *Journal*, page 347, the subtitle of the abstract of an article by Nayudamma *et al.* should read "I. The Effect of Some Salts in Sole Leather Tanning", not ". . . Chrome Leather Tanning".

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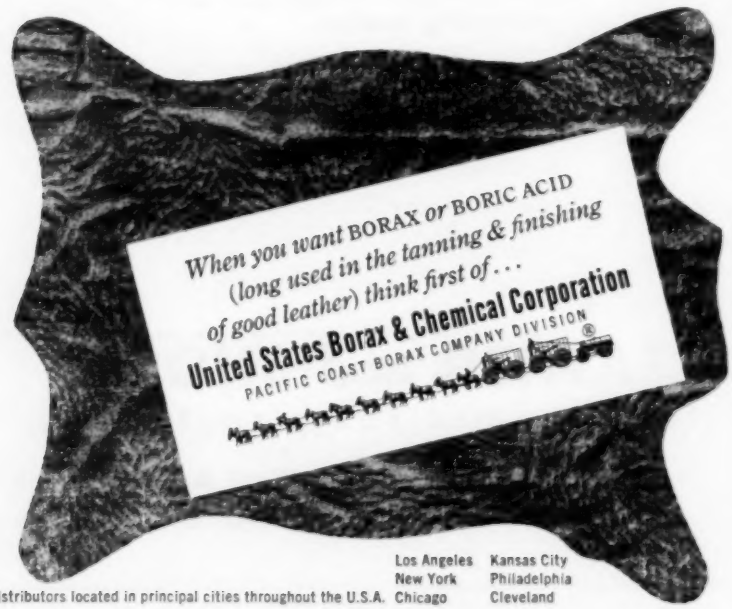
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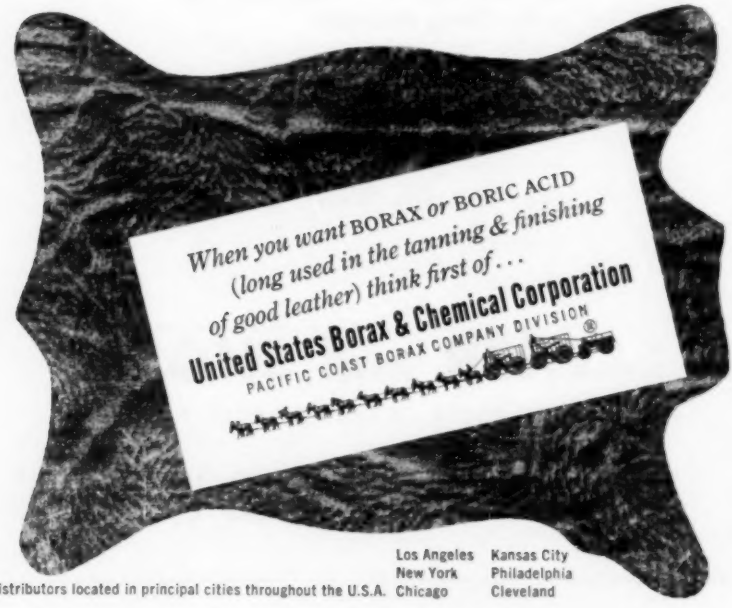
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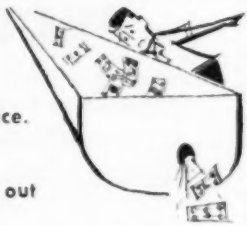

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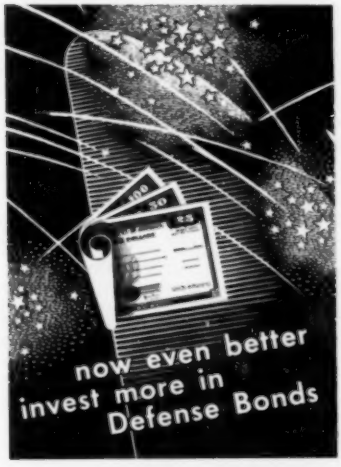

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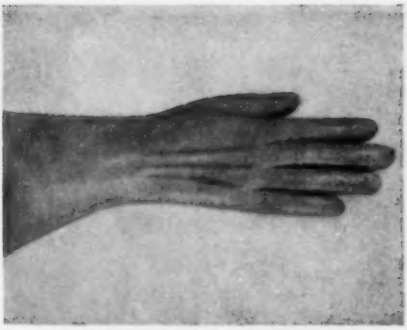
INDEX TO ADVERTISERS

ADOLF SCHUBERT XXIX
AMERICAN EXTRACT CO. XXIV
APEX CHEMICAL CO., INC. XXIV
ARKANSAS COMPANY, INC. VI
ARTHUR C. TRASK CO. XXVII
ARTHUR THOMAS CO. XVIII
ATLAS REFINERY XIV
AULSON TANNING MACHINERY CO., THE XXIX
A. W. HOPTON XXX
BARKEY IMPORTING CO., INC. ..... V — XII
BARRENTAN CORPORATION XXIV
BARIUM REDUCTION CORPORATION XIII
BONA ALLEN, INC. XXXII
BUCKMAN LABORATORIES, INC. IV
CHEMTAN COMPANY ..... Outside Back Cover
CLINTON CORN PROCESSING COMPANY XXXII
E. F. DREW & CO., INC. XXX
EISENDRATH TANNING CO. XXIII
FRANK F. MARSHALL XXVII
GARDEN STATE TANNING INC. XXVII
GEIGY COMPANY, INC. IX
GENERAL DYESTUFF COMPANY XI
HOOKER ELECTROCHEMICAL CO. XVII
HOWES LEATHER CO., INC. XXXII
KEPEC CHEMICAL CORPORATION XXVII
LEATHER AND SHOES XXI
LEATHER MANUFACTURER, THE XXXI
L. H. LINCOLN & SON, INC. XXV
LOWELL TECHNOLOGICAL INSTITUTE XXXIII
MARDEN-WILD CORPORATION XXVI
MUTUAL CHROMIUM CHEMICALS, ALLIED CHEMICAL & DYE CORP. ..... Inside Back Cover
NEWARK LEATHER FINISH CO. XXVIII
NOPCO CHEMICAL CO. XIX
OHIO LEATHER CO., THE XXIII
OLSON IMPORTING COMPANY, INC., THE ..... Inside Front Cover
ORTHMANN LABORATORIES, INC., THE XXIII
PRESTO COLOR CO. XXII
PROCTOR AND SCHWARTZ, INC. XXIX
REILLY-WHITEMAN-WALTON CO. XXXI
ROBESON PROCESS CO. II
ROHM & HAAS VIII
SALEM OIL & GREASE CO. XXVI
SAXE CUTCH CORPORATION XXX
SOLVAY PROCESS DIVISION, ALLIED CHEMICAL & DYE CORP. XV
SUN OIL COMPANY XXIII
TANIMEX CORPORATION III
TANNER'S COUNCIL RESEARCH LABORATORY ..... XXVII — XXX — XXXIII
UNITED STATES BORAX & CHEMICAL CORP. XXII
UNITED STATES TESTING COMPANY XXVIII
WALLERSTEIN COMPANY, INC. XX
WARNER CO. XXVI
WHITTEMORE-WRIGHT CO. XXII
WOLF, JACQUES & CO. VII
YOUNG CO., J. S. XVI



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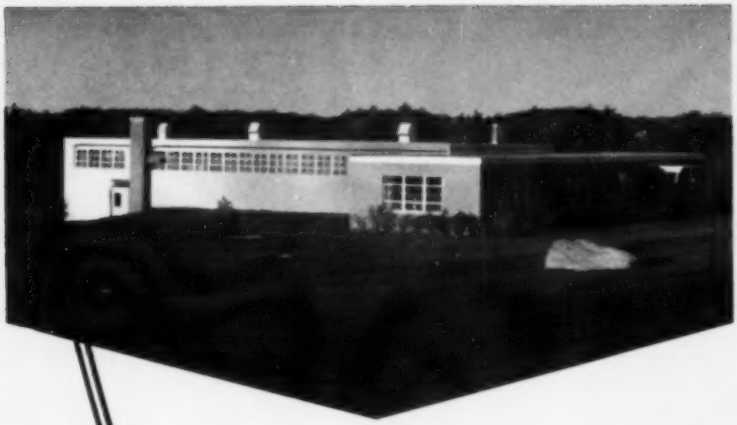

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